chloroform. The solution was heated quickly to reflux and retained at reflux for a total contact time of 10 min. It was then cooled, washed with water, and dried over magnesium sulfate, and the solvent was evaporated. IR analysis showed the carbonyl peak to have disappeared. The product was dissolved in 20 mL of benzene, Pd/C (5%, 0.2 g) was added, and the mixture was stirred under an atmosphere of hydrogen for 3 h and then filtered. VPC analysis (column B, 140 °C) showed peaks with retention times of 11.8 and 12.7 min in an area ratio of 96.5:3.5.

A second run was carried out by stirring the reaction mixture overnight at room temperature. After hydrogenation, VPC analysis showed peaks at t_R = 11.7 and 12.6 min in an area ratio of 94:6.

Reaction of Excess 2,6-Dimethylanisole with Allyl Chloride. Allyl chloride (0.75 g, 0.010 mol) was added to a mixture of 2,6-DMA (8.60 g, 0.0631 mol) and anhydrous zinc chloride (0.52 g, 0.038 mol) in 40 mL of chloroform. The mixture was heated at reflux for 18.5 h and cooled, and the solvent was evaporated. The residue was extracted with 1:1 benzene–petroleum ether, and the extract was washed twice with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent and excess 2,6-DMA were distilled off under vacuum to yield 0.30 g of a brown oily residue. VPC analysis on column A at 170 °C showed two peaks (t_R = 2.6 and 6.2 min) in an area ratio of 3.8:1. The major component was isolated by preparative VPC. Its NMR spectrum showed peaks at ca. δ 2.2 (4 peaks, 6 H), 3.1–3.4 (m, 2 H, allylic methylenes), 3.6 (s, 3 H, methoxy), and 4.7–5.3 (m, 2 H, terminal vinyl peaks), 5.5–6.3 (m, 1 H, secondary vinyl) and a 3-H signal consisting of a singlet at δ 6.85 overlapping doublets (*J* = 8 Hz) at δ 6.69 and 7.00. The spectrum corresponded to that expected of a mixture of 2-allyl- and 3-allyl-2,6-dimethylanisoles, but the ratio of isomers could not be determined.

In each of two later runs, the crude reaction product showed overlapping peaks at δ 5.8 and 6.2 (column B, 110 °C) but no products with higher retention times. The mixture in each case was dissolved in 10 mL of benzene and stirred under an atmosphere of hydrogen in the presence of 5% Pd/C (0.23 g) for 18 h. Filtration of the solution and evaporation of the solvent left a yellow oil whose NMR spectrum corresponded to that of a mixture of 3-propyl- and 4-propyl-2,6-dimethylanisoles. VPC analysis (column B, 100 °C) showed peaks (t_R = 5.5 and 6.8 min) in an area ratio of 40:60 in each run. Comparison with synthetic samples indicated the principal isomer to be 3-propyl-2,6-dimethylanisole.

Reaction of Excess 2,6-Dimethylanisole with Allyl Bromide. Allyl bromide (1.26 g, 0.104 mol) was added to a mixture of 2,6-DMA (7.34 g, 0.0539 mol) and anhydrous zinc chloride (1.04 g, 7.63 mmol) in 40 mL of chloroform. The mixture was heated at reflux for 19 h and worked up as described for the reaction with allyl chloride to yield 0.74 g of a yellow oil. VPC analysis (column A, 170 °C) showed peaks with retention times of 2.5 (corresponding to that expected for allyl dimethylanisoles), 5.0, 6.1, and 9.5 min. Isolation of the mixture of products with retention times of 5–6 min and of the product with the retention time of 9.5 min showed complex spectra lacking any vinyl peaks.

Part of the crude product (0.47 g) was dissolved in 20 mL of *tert*-butyl alcohol, and potassium *tert*-butoxide (0.54 g, 4.8 mmol) was added. The solution was heated at reflux for 21 h and cooled to room temperature, and petroleum ether was added. The mixture was washed twice with saturated ammonium chloride solution and dried over magnesium sulfate, and the solvent evaporated to yield 0.35 g of a yellow oil. VPC analysis (column A, 170 °C) showed two peaks (t_R = 2.9 and 3.2 min). The high retention time peaks previously present had essentially disappeared. The dehydrohalogenation product was dissolved in 15 mL of methanol, 0.2 g of 5% Pd/C was added, and the mixture was stirred at room temperature under an atmosphere of hydrogen for 8 days. It was then filtered, and the solvent was evaporated under vacuum to give 0.29 g of a pale yellow oil, whose NMR spectrum indicated the absence of vinyl peaks. VPC analysis (column B, 108 °C) showed two peaks with retention times of 5.9 and 7.0 min in an area ratio of 40:60. The hydrogenation product was dissolved in 10 mL of glacial acetic acid, and a solution of bromine (0.13 g, 0.81 mmol) in 5 mL of glacial acetic acid was added drop by drop. The resulting mixture was shaken for 5 min, and sodium sulfite solution was added. The mixture was extracted with petroleum ether, and the organic layer was separated and then washed with distilled water, 5% potassium hydroxide solution, and saturated ammonium chloride solution. It was then dried over magnesium sulfate and filtered, and the solvent was evaporated to yield 0.23 g of a yellow oil, which showed two major peaks (t_R = 1.18 and 7.1 min at 170 °C). These components were isolated by preparative VPC and identified as **2,6-dimethyl-4-propylanisole** and **4-bromo-2,6-dimethyl-3-propylanisole**.

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Registry No. **3a**, 83547-48-2; **3b**, 83547-44-8; **4a**, 13037-82-6; **4b**, 83547-45-9; **5a**, 83547-46-0; **5b**, 83547-47-1; **6**, 20700-88-3; 2,6-DMP, 576-26-1; 2,6-DMA, 1004-66-6; $ZnCl_2$, 7646-85-7; 3,5-dimethyl-4-methoxypropiophenone, 5384-11-2; 3-bromo-2,6-dimethyl-4-propylanisole, 83547-49-3; allyl chloride, 107-05-1; allyl bromide, 106-95-6; 2,6-dimethylphenol-*4-d*, 22100-63-6; 4-bromo-2,6-dimethylphenol, 2374-05-2.

On the Selectivity–Selectivity Relationship in the Solvolysis Reactions of Alkyl Halides

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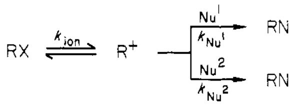
A recent common method for studying carbenium ion reactions and the nature of the solvolysis intermediates involves reactivity–selectivity plots.[1–7] The selectivities *S* are usually obtained from the product distributions in a competitive reaction of a cationoid species R^+ (which may be a free ion or an ion pair) with two nucleophiles Nu^1 and Nu^2 (eq 1), by application of eq 2.



$$\mathrm{RX} \underset{}{\overset{k_{\mathrm{ion}}}{\rightleftharpoons}} \mathrm{R}^+ \begin{cases} \xrightarrow[k_{\mathrm{Nu}^1}]{\mathrm{Nu}^1} \mathrm{RNu}^1 \\ \xrightarrow[k_{\mathrm{Nu}^2}]{\mathrm{Nu}^2} \mathrm{RNu}^2 \end{cases} \qquad (1)$$

$$S = k_{\mathrm{Nu}^1}/k_{\mathrm{Nu}^2} = [\mathrm{RNu}^1][\mathrm{Nu}^2]/[\mathrm{RNu}^2][\mathrm{Nu}^1] \qquad (2)$$

Two common pairs of nucleophiles Nu^1 and Nu^2 which give reactivity–selectivity plots are N_3^- and H_2O[2,3] and H_2O and EtOH.[4–6,7a] Sneen and co-workers[2] and Schleyer and co-workers[3] found that a plot of log k_{solv}, where k_{solv} is the solvolysis rate constant of an alkyl chloride in 80% acetone, against the corresponding log S_N = log ($k_{N_3^-}/k_{H_2O}$) for many alkyl chlorides is linear. This is a reactivity–selectivity relationship since k_{solv} is presumably proportional to the stability of the ion R^+ in its reactions with nucleophiles.

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Table I. S_E and S_N Values

no.	compd	S_E	log S_E	S_N, lit.[a]	S_N, cor[b]	log S_N, cor
1	$(p\text{-}MeC_6H_4)_2CHCl$	10.9 ± 2[c,d]	1.04	180[e]	227-1200[f]	2.4-3.08
2	1-(3-benzothienyl)ethyl acetate	5.81[g]	0.76		950[g]	2.98
3	Ph_2CHCl	3.25[h]	0.51	34	50 ± 1;[i] 96 ± 6[j]	1.7, 1.98
		(4.85)[d]	(0.69)		180 ± 20[k]	2.25 ± 0.05
4	$p\text{-}ClC_6H_4CH(Cl)Ph$	2.84[h]	0.45	56[l]	270[m]	2.4
		(8.0)[d]	(0.9)			
5	cyclopentyl-X	0.99[n]	0.0		240-630[o]	2.4-2.8
6	*exo*-2-norbornyl chloride	0.83[d]	−0.08	11	11	1.04
7	1-adamantyl-X	0.57[p,d]	−0.25	2.5[w,y]	2.5	0.4
		(0.84)[q]	(−0.075)		(20, 9)[r,y]	(1.30, 0.95)
8	Me_3CBr	0.43[s]	−0.37	74[t]	12[u]	1.08
9	2-adamantyl-X	0.166[p,d]	−0.78	1.7[w,z]	6.6[x]	0.82
		(0.33)[v]	(−0.48)		(32, 16)[r,z]	(1.51, 1.20)

[a] Literature value from ref 3. [b] Values calculated by us from the literature data using the appropriate corrections. [c] The actual value is probably much lower as judged by comparison of the data of ref 4 and ref 5a for other benzhydryl derivatives. [d] Data from ref 4, mostly in 70% EtOH. [e] Based on Ingold's data in 90% acetone.[10a] However, the $[H_2O]$ term was apparently forgotten when eq 2 was used. [f] Ingold found the same $[RN_3]/([ROH][N_3^-])$ ratio in 50-90% acetone,[10b] and Golomb[11] also found a relatively small dependence on $[H_2O]$. Our values are based on Ingold's values multiplied by the $[H_2O]$ term in 50-90% acetone. [g] Data from ref 12. [h] The value of ref 5a is more consistent with other data and with the expected higher selectivity of Ph_2CH^+ compared with $p\text{-}ClC_6H_4CHPh^+$. [i] From ref 10b and 13. [j] From ref 14. [k] For Ph_2CHBr from ref 15. [l] Based on data for the *p*-nitrobenzoate from ref 16. [m] Corrected for the formation of most of the RN_3 by acyl-oxygen fission. [n] Data for X = OBs from ref 17. [o] Data for X = OMs in 67% diglyme at various NaN_3 concentrations from ref 14. [p] For X = Cl. [q] For X = Br in 80% EtOH in the absence of NaN_3 (from ref 3). [r] Calculated from data of ref 3 in 75% dioxane in the presence of 0.06 and 0.1 M NaN_3, respectively. [s] The value is probably less accurate than other values since the amount of ROEt was determined by distillation and the amount of ROH was calculated from the difference, after correction for olefin formed.[18] [t] The value probably involves an error of 1 order of magnitude. [u] Corrected for the simultaneous elimination reaction. [v] For X = OTs in 80% EtOH in the absence of NaN_3 from ref 3. [w] Value in 80% EtOH from ref 3. The S_N values depend on the NaN_3 concentration. [x] Data in 70% acetone for X = OTs from ref 14. [y] For X = Br. [z] For X = OTs.

Harris and co-workers found a similar linear relationship between log (k_{EtOH}/k_{H_2O}) in 70% EtOH (log S_E) and log k_{solv} for alkyl chlorides in 80% acetone.[4b]

Pross and co-workers plotted recently log S_E against log S_N for several alkyl derivatives.[6] They obtained an approximate correlation[6b] with a unit slope[6a] for six compounds ranging in reactivity and selectivity from the 2-adamantyl to the di-*p*-tolylmethyl system. The points for the 1-octyl and the 2-octyl systems deviated from the line, and this was ascribed to product-forming step which differs from that for the other substrates. It was suggested that the correlation of the two alternative measures of selectivity "strongly reinforces the view that selectivity values are not arbitrary but signify the ability of a species to differentiate between different reagents".[1]

We note that the linearity of the two selectivity measures is not surprising. Since the plots of log S_N or log S_E against log k_{solv} (80% acetone) are both linear, a log S_E vs. log S_N plot *must be linear*. An approximate correlation reflects imperfections in the individual log k_{solv} vs. log S plots.

The use of a selectivity vs. selectivity plot may be advantageous since it involves rate constants related to the product-forming step and reactions of the intermediate and eliminates problems associated with its rate-determining formation. For example, ground-state effects on log k_{solv} or differences in log k_{solv} of isomeric precursors (e.g., allylic) which give the same R^+ do not affect the log S_E vs. log S_N plot. On the other hand, a deviation in k_{solv} for a certain RX from the log k_{solv} vs. log S_N plot which may have a mechanistic significance may be lost in the linear log S_E vs. log S_N plot. Experimental errors in the log k_{solv} vs. log S plots can be sometimes amplified in the log S_E vs. log S_N plot, giving artifacts.

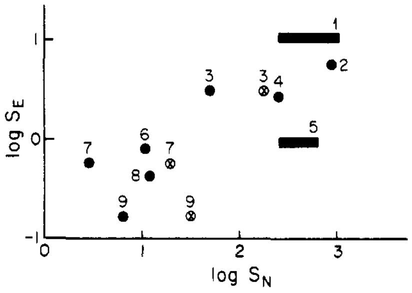

Figure 1. Selectivity (log S_E) vs. selectivity (log S_N) plot for cationoid species derived from the solvolysis of RX. Points indicated by ⊗ are for the same compounds as points indicated by ● except that the highest S_N values were used for the former.

However, the reported slope of unity in the log S_E vs. log S_N plot is surprising since it leads to a result in contrast with the reactivity–selectivity principle which is the basis of the log k_{solv} vs. log S plots. The S_N values which were used for the log k_{solv} vs. log S_N plot were measured in a variety of aqueous–organic solvents (e.g., $H_2O\text{–}Me_2CO$, $H_2O\text{–}EtOH$), implying that they are nearly solvent independent. Hence, a linearity of log S_E vs. log S_N with a unit slope leads to eq 3, with the consequence that the selec-

$$\log (k_E/k_W) = \log (k_N/k_W) + \text{constant} \qquad (3)$$

tivity ratio k_E/k_N is constant and independent of the nature of R^+. A "constant selectivity" for a pair of nucleophiles, while two related S values change on changing R^+, seems highly unlikely.

We believe that the discrepancy is due both to the assumption of the solvent independence of the S_N value and to the use of inaccurate literature S_N (and some S_E) values in the log k_{solv} and log S_E vs. log S_N plots. A reanalysis of the log k_{solv} vs. log S_N plot[8] suggests that several of the S_N values should differ from those previously used.[3,6] The literature values together with our corrected S_N values are given in Table I. The footnotes explain the reasons (e.g., neglect of side reactions or of the $[H_2O]$ term) why the corrections were introduced. A plot of log S_E vs. log S_N values (Figure 1) which includes some points which did not appear in Pross' plot[6] shows a large uncertainty and a scatter of the points rather than the reported linearity. Indeed, due to the large scatter of the points for benzhydryl

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(log S_E = 0.51–0.69; log S_N = 1.7–2.3), 1-adamantyl (log S_E = −0.075 to −0.25; log S_N = 0.4–1.30), and 2-adamantyl (log S_E = −0.48 to −0.78; log S_N = 0.82–1.51), we arbitrarily plotted in Figure 1 the points corresponding to the lowest S_N values. However, we also added the points with the highest S_N values for these compounds (see Table I) in order to demonstrate the uncertainty in the values.[9]

Our conclusion is that by use of the presently available data the selectivity–selectivity plot shows a scatter of points rather than being linear. If a linearity is enforced on the plot, the "best" slope is lower than unity. Whether a mechanistic conclusion concerning the product-determining step for various R^+'s can be drawn from such a plot is not clear.[19]

Acknowledgment. This research was supported by the Israel commission for Basic Research, the Israel Academy for Sciences and Humanities, to which we are indebted.

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(19) We want to emphasize that the purpose of this paper is not to criticize previous workers who based their correlations mainly on literature data from various sources. We have three aims: (a) to point out that the linearity of the log S_E vs. log S_N plot does not give additional information over that already embodied in the log S_N and log S_E vs. log k_{solv} plots; (b) to point out the inherent inconsistency in a slope of unity for the log S_E vs. log S_N plot; (c) to offer an explanation to point b. Other explanations, e.g., different extents of capture of different cationoid species (free ions, ion pairs), are also possible.

Convenient Preparation of Carbonates from Alcohols and Carbon Dioxide

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Various routes are available to produce dialkyl carbonates, but, except for the chloroformate approach (eq 1),

$$\mathrm{ROCOCl + ROH + NaOH \rightarrow ROCOOR + NaCl} \qquad (1)^{1}$$

$$\mathrm{ROCOO^{-}Na^{+} + RX \rightarrow ROCOOR + NaX} \qquad (2)^{2}$$

$$\mathrm{2ROH + CO + 0.5O_2 \xrightarrow[R'_3N,\ 4\ atm]{Cu_2Cl_2} ROCOOR + H_2O + R'_3N{\cdot}HCl} \qquad (3)^{3}$$

$$\mathrm{2ROH + NH_2CONH_2 \xrightarrow[\substack{Dibal\\ 150\text{–}200\ ^\circ C}]{Ph_3P} ROCOOR + 2NH_3} \qquad (4)^{4}$$

$$\mathrm{ROH + CO_2 \xrightarrow[R'_3N,\ \Delta]{} ROCOOR} \qquad (5)^{5}$$

they usually result in low conversions making them inconvenient for laboratory preparations. Moreover, oxidative conditions (eq 3) and high temperatures (eq 4) are frequently incompatible with remote functionalities, as are the strong bases favored in the chloroformate route. These conditions are imposed to overcome or avoid the especial instability of the hemicarbonic acids, which otherwise might be viewed as simple carboxylic acids, subject to ordinary esterification conditions.

Table I

starting alcohol	reaction[b]		product
	method	yield,[a] %	
1-pentanol	A	88 (81)	dipentyl carbonate
2-butanol	A	80 (47)	di-*sec*-butyl carbonate
2-ethylhexanol	A	74 (45)	bis(2-ethylhexyl)-carbonate
2-ethylhexanol	B	97 (61)	bis(2-ethylhexyl)-carbonate
allyl alcohol	A	75 (40)	diallyl carbonate

[a] By GC analysis, based on unrecovered alcohol. Values in parentheses are isolated yields, after column chromatography. Most of the differences are due to losses during evaporative workup. [b] Reaction time was 18 h in all cases.

The view of carbonate formation as esterification of hemicarbonic acid led me to consider application of the conditions first described by Mitsunobu and Eguchi[6a] in 1971. Their preparation of carboxylic esters from alcohols, carboxylic acids, triphenylphosphine (Ph_3P), and diethyl azodicarboxylate (DEADC) in tetrahydrofuran (THF) solution is characterized by mildness, simplicity, and high yields. The net effect of the reaction is displacement of the alcoholic hydroxyl group, and the displacement has been accomplished by imides,[6b] phenols,[6c,e] and other species,[6f] having $pK_a < 10$ and solubility in THF.

Hemicarbonic acids fit these latter requirements, and I now report that they undergo esterification, affording carbonates in good yield under ambient conditions. The

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