Compound **4c**: syrup; 57% yield; NMR (CCl_4 δ 1.95 (s, 3 H), 1.6–2.2 (m, 2 H), 2.42 (t, 2 H), 3.25 (s, 6 H), 4.00 (d, 2 H), 4.30 (t, 1 H), 7.10 (br t, 1 H); MS, *m/e* 173, 172 (M − MeO), 171, 158, 157, 156, 142, 141, 140, 131, 129, 116, 115, 114, 103, 102, 101, 100, 99, 98. Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.11; H, 8.19; N, 6.92.

The preparation of compounds **4a** and **4b** in quantities up to 0.5 mol can readily be achieved by using the same procedure as described above except that the products are purified by distillation with a short-path distillation apparatus. The yields (50–60%) are slightly lower than those obtained as described above.

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Registry No. 3a, 4220-66-0; **3b**, 25252-24-8; **4a**, 82614-43-5; **4b**, 3209-78-7; **4c**, 82614-44-6; **5a**, 88-14-2; **6a**, 623-17-6; **6b**, 534-22-5; **6c**, 5663-62-7; *cis*-**7a**, 82614-40-2; *trans*-**7a**, 82614-45-7; *cis*-**7b**, 82614-41-3; *trans*-**7b**, 82614-46-8; *cis*-**7c**, 82614-42-4; *trans*-**7c**, 82614-47-9; 2-methyl-3-furoic acid, 6947-94-0; *cis*-2-(acetoxymethyl)-2,5-dimethoxy-2,5-dihydrofuran, 38588-84-0; *trans*-2-(acetoxymethyl)-2,5-dimethoxy-2,5-dihydrofuran, 38588-85-1.

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Communications

S_N2 Reactions of Carbanions with Primary and Secondary Alkyl Bromides in Dimethyl Sulfoxide Solution

Summary: 9-Methylfluorenyl carbanions undergo S_N2 reactions with cyclohexyl, isopropyl, isobutyl, and *n*-butyl bromides in high yields in Me_2SO solution with the relative rates of (1.0), 6.4, 8.6, and 56 respectively.

Sir: Although the S_N2 reaction has probably received more attention from organic chemists than any other reaction type, very little quantitative information is available concerning carbanions as nucleophiles. Rate studies have been limited largely to weakly basic enolate ions, such as those derived from β-keto esters, where counterion effects complicate interpretations. More strongly basic carbanions can be generated in hydroxylic solvents only in small and unknown concentrations. For synthetic purposes, high concentrations of strongly basic carbanions are routinely generated in weakly acidic solvents that have a low dielectric constant, such as tetrahydrofuran, but here counterion effects become very strong. The establishment of acidity scales in the strongly dipolar nonhydroxylic ("aprotic") solvents, dimethyl sulfoxide[1] and *N*-methylpyrrolidin-2-one,[2] has provided a groundwork for the generation of carbanions of a wide range of basicity in known concentrations, free of counterion effects. In earlier papers we have reported the results of S_N2 reactions for several families of carbanions reacting with $PhCH_2Cl$;[3] other primary alkyl halides have also been studied.[4] In this communication we report the extension of these studies to cyclohexyl bromide, c-$C_6H_{11}Br$, and isopropyl bromide.

The rates of reactions of these secondary alkyl bromides with carbanions from the 9-methylfluorenyl carbanion family, 9-Me-Fl$^-$,[3] were found to be first order in each reactant. Substitution was the predominant course of reaction with elimination playing a minor role. Formation of only small amounts of elimination products was at first sight surprising since these carbanions are strongly basic and it has been shown that with strongly basic sodium-enolate ion pairs, elimination may become the major reaction with secondary, and even primary, halides in polyether solvents.[5] Also, c-$C_6H_{11}Br$ has been singled out as being particularly prone to elimination.[6] For example, reactions of c-$C_6H_{11}Br$ with NaOEt/EtOH or *t*-BuOK/*t*-BuOH give exclusively elimination.[7] In acetone or dimethylformamide, most anions (Cl^-, Br^-, AcO^-, ArO^-, CN^-, and HCO_2^-) give more elimination than substitution; azide ion alone gives more S_N2 than E2.[7] (Similar results were obtained with c-$C_6H_{11}I$ and c-$C_6H_{11}OTs$.) As a consequence, it is generally assumed that S_N2 reactions of c-$C_6H_{11}X$ substrates with nucleophiles are subject to some kind of rate retarding steric effect,[8] and that elimination becomes predominant for that reason.

Examination of the literature revealed, however, that reactions of carbanions with c-$C_6H_{11}Br$ often give unusally high yields of substitution products, e.g., 40% for $[Ph_2CC{\equiv}C]^{2-}2M^+$ in NH_3,[9] 76% for $NaCH(CO_2\text{-}t\text{-}Bu)_2$ in *t*-BuOH,[10] 65–77% for PhCH(Na)CN in $PhCH_3$,[11] and 82% for 2-lithio-2*H*-thiopyran in NH_3.[12] Our studies using equimolar amounts of 9-MeFl$^-$ or of 9-$PhCH_2Fl^-$ carbanions with c-$C_6H_{11}Br$ in Me_2SO gave 80% or more of substitution product (Table I).

These synthetic results show that large, delocalized, strongly basic carbanions are remarkably effective in promoting S_N2 reaction in preference to E2 reactions with c-$C_6H_{11}Br$. Their behavior in this respect is in sharp contrast to that of the CN^- ion, which is 9.45 p*K* units less basic than 9-MeFl$^-$ in Me_2SO, but reacts with c-$C_6H_{11}Br$ in acetone at 75 °C to give 92% elimination.[7] The relative insensitivity of 9-MeFl$^-$ ions to increasing steric hindrance

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Table I. Relative Rates of S_N2 Reactions of Alkyl Bromides with Iodide Ions, Azide Ions, and 9-Methylfluorenyl Ions in Strongly Dipolar Nonhydroxylic Solvents

alkyl bromide	$I^-(Me_2CO)$[a] (60 °C)	$N_3^-(DMF)$[c] (25 °C)	$9\text{-MeFl}^-(Me_2SO)$[d] (25 °C)	$2,7\text{-Br}_2\text{-9-MeFl}^-$ (Me_2SO, 25 °C)
n-BuBr	3000[b]	200	56[e]	97
i-BuBr	230	10	8.5[f]	
i-PrBr	40	40	6[g]	10
$c\text{-}C_6H_{11}Br$	(1.0)	(1.0)	(1.0)[h,i]	(1.0)[j]

[a] Schotsman, L; Fierens, P. J. C. *Bull. Soc. Chim. Belg.* **1959**, *68*, 580-598. [b] For *n*-PrBr. [c] Alexander, R.; Ko, E. C. F.; Parker, A. J.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049-5069. [d] Product studies were carried out, unless otherwise noted, by reacting equimolar quantities of 9-G-Fl^- and RBr at room temperature for several days. The percent of 9-G-FlH in the crude solid product (NMR analysis) was used to estimate the amount of elimination. Satisfactory C and H and mass spectral analyses were obtained on the purified substitution products. [e] Reference 4. [f] $9\text{-PhCH}_2\text{-9-}i\text{-BuFlH}$ (85%), mp 85.5-87 °C, was obtained (10% elimination). [g] Reaction with excess *i*-PrBr gave 83% 9-Me-9-*i*-Pr-FlH, mp 39-41 °C. [h] $9\text{-Me-9-c-}C_6H_{11}FlH$ (80%), mp 171-172 °C, was obtained (15% elimination); $9\text{-PhCH}_2\text{-9-c-}C_6H_{11}FlH$ (85%), mp 107.5-108.5 °C, was obtained (15% elimination). [i] The rates were determined by the method described previously;[3] $k = 0.280 \pm 0.008\ M^{-1}\ s^{-1}$. [j] $k = 0.0290 \pm 0.001\ M^{-1}\ s^{-1}$. The pK_a values for 9-MeFlH and $2,7\text{-Br}_2\text{-9-MeFlH}$ are 22.3 and 17.7, respectively.

in alkyl bromides is brought out further in Table I by rate comparisons with I^- and N_3^- ions, which are powerful nucleophiles. We see that the 9-MeFl^- ion, despite its large size and seemingly less accessible reaction site, appears to be actually *less* sensitive to structural effects in RBr that retard S_N2 reactions for steric reasons than are I^- or N_3^- ions. Whereas *β*-methyl branching (*i*-BuBr vs. *n*-Br) retards the rate of reaction with I^- by 13-fold and that with N_3^- ion by 20-fold, the retarding effect for 9-MeFl^- ion is only 6.5-fold. For *α*-methyl branching (*i*-PrBr vs. *n*-BuBr) the retarding effects are 75-fold for I^-, 5-fold for N_3^-, and 9-fold for 9-MeFl^-. Finally, the retarding effect for $c\text{-}C_6H_{11}Br$ is 3000-fold for I^-, 200-fold for N_3^-, and 56-fold for 9-MeFl^-.

The variation in sensitivities of 9-MeFl^-, N_3–, and I^- to changes in alkyl bromide structure (Table I) once again emphasizes the importance of the nature of the donor atom in determining anion reactivities.[3] It is necessary to try to make comparisons of anion reactivities of the same basicity, however, before drawing conclusions concerning the reasons for this variation. Each substrate has a different sensitivity to changes in basicity as defined by the Brønsted *β*. For example, for reactions of 9-MeFl^- anions with *n*-BuBr, *i*-PrBr, and $c\text{-}C_6H_{11}Br$, the *β* values are 0.365, 0.38, and 0.42, respectively. The appreciable difference in *β* values for *n*-BuBr and $c\text{-}C_6H_{11}Br$ causes the $n\text{-BuBr}/c\text{-}C_6H_{11}Br$ rate ratio to change from 56/1 for 9-MeFl^- to 97/1 for $2,7\text{-Br}_2\text{-9-MeFl}^-$, which is 4.6 p*K* units less basic (Table I). If we use these *β* values to extrapolate the $n\text{-BuBr}/c\text{-}C_6H_{11}Br$ rate ratio for reactions with 9-MeFl^- down to a basicity equal to that of the conjugate acid of N_3^- in Me_2SO (7.7), the ratio increases from 56 to about 350. Further extrapolation down to a basicity equal to that of the conjugate acid of I^- in Me_2SO (~0) causes the ratio to increase to about 1000. This suggests that although the data at first glance indicate a lesser sensitivity of 9-MeFl^- than I^- or N_3^- ions to the retarding effects of *α*- and *β*-alkyl branching, these anions are probably all responding in a similar manner. We conclude that size and extent of delocalization are not important factors in determining the sensitivities of anions to the retarding effects of *α* branching in alkyl bromides on S_N2 reactions.

The *β* values are also important in determining the effect of a change in basicity of the anion on the $E2/S_N2$ rate ratio. For ArS^- ions reacting with $c\text{-}C_6H_{11}Br$ in EtOH the *β* values for E2 and S_N2 reactions are 0.36 and 0.32, respectively,[13] and for ArO^- ions reacting with 4-bromoheptane in EtOH they are 0.39 and 0.27, respectively.[14] If the E2 reactions for sodium enolate ions reacting with alkyl halides in polyether solvents have larger *β* values than the S_N2 reacitons, this would explain, in part, the sharp increase in the percentage of eliminatin with increasing enolate ion basicity.[5,15]

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Registry No. 9-PhCH_2Fl^-, 53629-11-1; 9-MeFl^-, 31468-21-0; $2,7\text{-Br}_2\text{-9-MeFl}^-$, 73872-46-5; *n*-BuBr, 109-65-9; *i*-BuBr, 78-77-3; *i*-PrBr, 75-26-3; $C\text{-}C_6H_{11}Br$, 108-85-0; $9\text{-PhCH}_2\text{-9-}i\text{-BuFlH}$, 82571-46-8; 9-Me-9-*i*-PrFlH, 57645-03-1; $9\text{-Me-9-c-}C_6H_{11}FlH$, 82571-47-9; $9\text{-PhCH}_2\text{-9-c-}C_6H_{11}FlH$, 82571-48-0; PhC(ONa)=CHPh, 82571-49-1; PhC(ONa)=CHEt, 17003-51-9.

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[15] For *i*-PrBr, changing the base from PhC(ONa)=CHPh to PhC(ONa)=CHEt caused the percentage of elimination to increase from 7% to 88% in the polyether solvent.[5] The basicity increase for the ion pairs (or ion aggregates) was estimated to be 2.5 units. In Me_2SO, where free enolate ions are involved, the change would be about 7 p*K* units.[16] Differences in steric and ion pairing effects, as well as basicity, may of course also influence the percentage of elimination.

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On the Addition of Allyltrimethylsilane to Glycal Acetates

Summary: A highly stereoselective route to C_1 allylated glycosides bearing C_2–C_3 unsaturation has been developed.

Sir: Recently a very simple entry to 5,6-dihydro-γ-pyrones (1) was found.[1-4] By this methodology the relative configurations about C_5 and C_6 of the heterocycle[5] and even C_7 of a pendant side chain are subject to considerable control.[3-4] The resultant pyrones are readily converted in a stereoselective way to glycals of the type **2**.[6] Through

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