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Benzylic Organolithium Carbanion Reactivity. 3. Kinetic Studies with Neopentyl Halides and Benzyl Fluoride

Sir:

Benzylic organolithium reagents couple rapidly with benzylic chlorides and more slowly with benzylic fluorides to give phenylated ethanes in 91–97% yields.[1] In coupling reaction competition experiments at 25 °C, mixtures of Ph_2CHF and $PhCH_2F$ showed a normal steric hindrance to displacement effect. A kinetic investigation of the coupling reactions of triphenylmethyllithium (**1**) and diphenylmethyllithium (**4**) with benzyl fluoride and neopentyl halides was begun in order to establish the rate law for the process. These halides were chosen because they are structurally incapable of undergoing elimination of HX and for their convenient rates. Now we can report that the coupling reactions of **1** and **4** with neopentyl iodide (**2a**) and neopentyl bromide (**2b**), as well as with benzyl fluoride, follow second-order rate laws and exhibit steric and halogen kinetic effects characteristic of conventional S_N2 processes.

Neopentyl iodide reacts with 0.1–0.32 M tetrahydrofuran (THF) solutions of tritylithium to give 3,3-dimethyl-1,1,1-triphenylbutane[2] (**3**) in 85–95% yields in preparative as well as in kinetic runs (eq 1). Benzhydryllithium (**4**) couples similarly with **2a** or **2b** to give 3,3-dimethyl-1,1-diphenylbutane[3] (**5**) (eq 2) in high yields. Both of these reactions exhibit second-order kinetics overall with first-order dependence on both the organolithium and the alkyl halide. This was demonstrated by observing the pseudo-first-order decay of **1** and **4** in the presence of excess of either reactant.

$$\underset{\mathbf{1}}{Ph_3CLi} + XCH_2C(CH_3)_3 \xrightarrow{THF} \underset{\mathbf{3}}{Ph_3CCH_2(CH_3)_3} \quad (1)$$

2a, X = I
b, X = Br
c, X = Cl (no reaction)

$$\underset{\mathbf{4}}{Ph_2CHLi} + \underset{(\mathbf{a}\text{ or }\mathbf{b})}{\mathbf{2}} \xrightarrow{25\ °C} \underset{\mathbf{5}}{Ph_2CHCH_2(CH_3)_3} \quad (2)$$

In kinetics runs where the concentrations of RLi and R′X are comparable and range from 0.08 to 0.29 M, second-order rate constants were secured for eq 1 and 2 from plots that are linear to 80% conversion or better by least-squares analysis. For each kinetic run, the rates of disappearance of **1** or **4** and **2a** or **2b** were measured and are represented as k_{RLi} and $k_{R'X}$ for comparison with the rate of formation of the hydrocarbon coupling product (k_{hc}).[4] The purpose of this approach is to monitor side reactions of RLi with the solvent and alternative reaction paths such as carbenoid formation. For the reaction of **1** with **2a** at 25.0 °C, the k values ($\times 10^{-3}$ L mol^{-1} s^{-1}) are as follows: $k_{RLi} = 3.3 \pm 0.13$; $k_{R'X} = 3.2 \pm 0.10$; and $k_{hc} = 2.7 \pm 0.25$. Thus formation of $(CH_3)_3CCHLiX$ is not as significant for reaction of **1** with **2a** at 25 °C as it is at 40 °C where reactant disappearance rates are almost twice as great as the coupling product formation rate.

Furthermore, in the coupling reaction of 0.03 M **1** with 0.03 M benzyl fluoride, (**6**) to give 64–74% yields of *unsym*-tetraphenylethane (**7**), formation of PhCHLiF is $\frac{1}{4}$ to $\frac{1}{3}$ as fast as coupling, as shown by the isolation of *trans*-stilbene.[5] The rate of formation of **7** ($k_{hc} = 0.074 \pm 0.03$ M^{-1} s^{-1} at 0 °C) is substantially higher than we indicated earlier.[7]

The rate constants k_{hc} for the coupling reaction of **1** and **2a** at 0, 25, and 40 °C give a good Arrhenius plot with $\Delta H = 15.5$ kcal/mol and $\Delta S = -23.1$ cal/(mol deg). These results show that the sterically hindered ion-pair nucleophile (**1**) reacts at a substantial rate with neopentyl halides **2a** and **2b** by a process whose energy parameters compare favorably with those expected for a polar process.[8] In contrast **1** reacts with triphenylmethyl chloride by an electron-transfer process.[1b]

Analysis of the rate constants in Table I for diphenylmethyllithium coupling reactions with alkyl halides shows that neopentyl iodide couples with diphenylmethyllithium 6.5 times faster than neopentyl bromide. A recent literature value for the same element effect rate ratio for the reactions of **4** with isopropyl iodide and bromide is 25.8 (uncorrected for the elimination reaction).[9] Thus the reactivity ratio obtained here agrees quite well with that found for well-recognized S_N2 reactions, rather than with values reported for radical-anion rate ratios.[9b] In addition, an alkyl group steric effect of 10^{-6} is found for the rate difference between neopentyl bromide and *n*-hexyl bromide.

That **1** and **4** react by a normal S_N2 mechanism with **2a** and **2b** is supported by the inversion of configuration of chiral α-phenylethyl chloride during coupling with diphenylmethyllithium[10] together with the known inversion of configuration in chiral neopentyl-*1-d* tosylates and halides during displacements with a variety of nucleophiles.[11]

Neopentyl iodide reacts with Ph_2CHLi to produce a bimolecular coupling product 8.5 times faster than Ph_3CLi. At first sight this result seems lower than expected in that Ph_2CHLi is 100 times stronger as a base than Ph_3CLi ($pK_a = 33.5$ for Ph_2CH_2 vs. 31.5 for Ph_3CH).[12] However, tritylithium in THF exists 100% as solvent-separated ion pairs,[13] while

Table I. Rate Constants for the Reaction of Diphenylmethyllithium with Alkyl Halides

no. of runs	R–X (concn, M)	$[Ph_2CHLi]$, M	k, L mol^{-1} s^{-1} at 25 °C		
			k_{RLi}	$k_{R'X}$	k_{hc}
1	*neo*-C_5H_{11}–I (0.094)	0.084	2.82×10^{-2}		2.33×10^{-2}
2	*neo*-C_5H_{11}–Br (0.175)	0.167	3.63×10^{-3}	3.68×10^{-3}	3.55×10^{-3}
ref 9	*n*-C_6H_{13}–Cl		1.0×10^{1}		
ref 9	*n*-C_6H_{13}–Br		2.7×10^{3}		
ref 9	*i*-C_3H_7–Br		1.9×10^{2}		
ref 9	*i*-C_3H_7–I		4.9×10^{3}		

Ph_2CHLi is a solvent-dependent equilibrium mixture of contact-ion and solvent-separated ion pairs[14] as shown by UV,[15] NMR,[14] conductivity,[15] and kinetic studies.[13,16] Therefore the constants reported in Table I are apparent rate constants or composites of the rate constants k_c and k_s for the two kinds of ion pairs in **4**.[16]

Preliminary attempts to determine rate constants at 0.0 °C for the reaction of **4** with neopentyl iodide in THF gave values that are comparable in magnitude with rates obtained at 25 °C. Presumably this is due to an increase in the proportion of the more reactive solvent-separated ion pair at lower temperatures.[13,16]

Although neopentyl chloride does not react with **1** or **4** to give a coupling product, it does give Ph_3CH and Ph_2CH_2 and probably the carbenoid. By contrast neophyl chloride ($PhC(CH_3)_2CH_2Cl$) couples with **4** to give 1,1,3-triphenyl-3-methylbutane (52.6%)[17] without evidence for the presence of a rearranged coupling product.

In summary we conclude that **1** and **4** react with neopentyl bromide, neopentyl iodide, and benzyl fluoride following second-order rate laws and exhibiting S_N2-like alkyl group and element effects on coupling reaction rates.

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(5) Stilbene probably comes from α-fluorobibenzyl either by in situ dehydrohalogenation with Ph_3CLi or by thermal elimination of HF in the injection port of the gas chromatograph.[6] The formation of α-fluorobibenzyl occurs by a scheme like that known for benzyl chloride's reaction with *n*-butyllithium.[6]

$$Ph_3CLi + PhCH_2F \rightarrow PhCHFLi \xrightarrow{PhCH_2F} PhCHFCH_2Ph + LiF$$

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A Facile Ring-Opening Reaction of Furfuryl Carbanion. Regioselective Generation of Di- or Trianionic Enolates

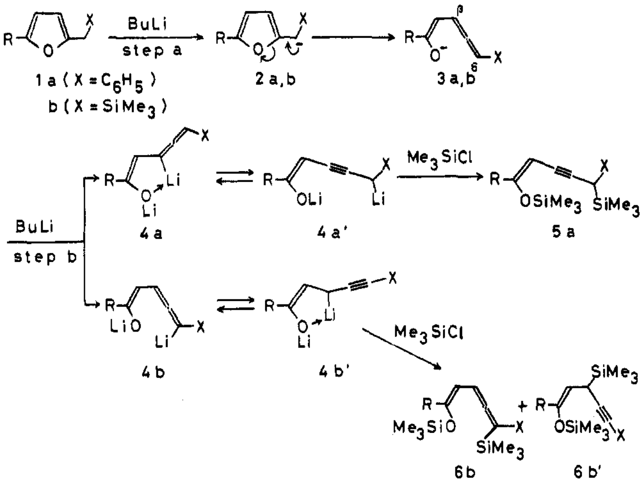
Sir:

Furan derivatives are well known to undergo ring-opening reactions under acidic conditions and have widely been employed as excellent precursors of 1,4 diketones.[1] However, they are usually quite stable under basic conditions because of the π-electron excessive character of furan ring.

We have recently reported ring-opening reactions of furan derivatives under the influence of metallic sodium and chlorotrimethylsilane; 2-furancarboxylic esters[2] and 2-furaldehyde diphenyl thioacetals[3] are converted into the corresponding acyclic silyl enol ethers. In these reactions, 2-furfuryl carbanion **2** was postulated to be a key intermediate for ring opening. In the course of mechanistic studies, it has been proved that a facile ring cleavage of furan takes place through **2** to yield allenic enolate **3**[4] on treatment of a furan having an anion stabilizing group with butyllithium. With the resulting enolate **3**, it has also been found that lithiation of the allenic hydrogen[5] is further effected very easily to yield the corresponding dianionic enolate **4.** However, examination of the silylated products revealed a marked contrast; **1a** afforded **5a**[6] as a sole product through selective removal of β hydrogen, while the δ hydrogen was lithiated preferentially to yield **6b**[7] and **6b'**[8] from **1b.**

In each case, the geometry of the enol double bond was confirmed to be *Z* exclusively,[9] as expected from the furan ring. Further, in this successive lithiation reaction, the second step, b, appears to proceed much more rapidly than the lithiation of the starting furan derivative (step a) (Scheme I). For example, an equimolar reaction of 2-benzylfuran (**1a**, R = H) with butyllithium was accompanied by recovery of the starting material (50%), giving disilylated product **5a** (R = H) in 42% yield. The following procedures are illustrative. To a solution of 2-benzylfuran **1a** (R = H) (0.310 g, 2 mmol) was added a solution of butyllithium (4 mmol) at −78 °C. Then the solution was warmed to 0 °C and stirred for 10 min. After the solution was cooled again to −78 °C, chlorotrimethylsilane (0.76 mL, 6 mmol) was added and the mixture was stirred for 2 h at room temperature. The reaction mixture was poured into an ice-cooled saturated aqueous $NaHCO_3$ solution and this mixture was then extracted with hexane. The crude product was distilled to give 0.513 g (85%) of the *Z* isomer of the silyl enol ether of 5-phenyl-3-trimethylsilyl-4-pentyn-1-al (**5a,** R = H). See Table I.

Scheme I



With 3 equiv of butyllithium, trianionic enolate can also be generated efficiently; silylation and acidic hydrolysis of the