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Notes

Reaction of Poly(styryllithium) with Tetrahydrofuran

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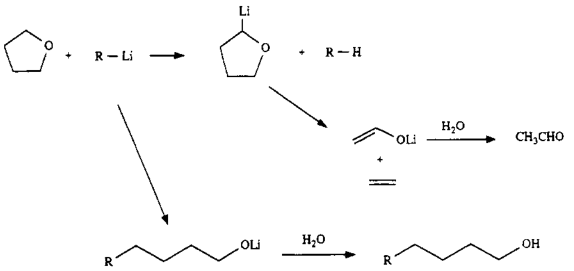
Introduction

Organolithium compounds are generally aggregated, usually as hexamers, tetramers, and dimers whether in the solid state,[1] gas phase,[2] or solution.[3] Ethereal solvents can have a tremendous effect on organolithium compounds, changing both their structure and reactivity. They may increase the reactivity by a million fold or more. Basic solvents tend to decrease the state of aggregation of organolithium reagents, with less aggregated organolithiums generally being more reactive.[4] Lower aggregation states are certainly responsible in part for the activation observed in basic solvents as has been noted with *n*-butyllithium.[5] Forceful arguments based on chemical computations have been presented that suggest that the effect is a transition state effect.[6]

Similar behavior is observed for benzyllithium and substituted benzyllithium reagents. Poly(styryllithium), like benzyllithium, is known to be a dimer in hydrocarbon solvents. In THF, the solvent breaks apart the dimer, giving unassociated poly(styryllithium) as the predominant species.[7] Poly(styryllithium), in THF, is a much more reactive propagating species than poly(styryllithium) in benzene. In fact, it has been proposed that poly(styryllithium) in dioxane and THF solvents tends to propagate principally through a small amount of very reactive solvent-separated ion pairs or free ions, respectively.[8]

The main problem associated with basic solvents is their inherent reactivity toward the alkyllithium reagents.[9] These reagents eventually metalate and/or are alkylated by the solvent. THF is a powerful ethereal solvent but is also particularly susceptible to reaction with strong bases.[10,11] The reaction of alkyllithium reagents with THF has been reported several times in the literature.[12–14] Ethyllithium has been reported to react with THF to give ethylene, acetaldehyde, and hexanol (1; R = Et) after quenching with water (eq 1).[13] *n*-Butyllithium has been shown to react rapidly with THF at room temperature to give ethylene and lithium enolate, although no addition product, *n*-octanol (1; R = *n*-Bu), was found.[14]



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(1)

In our recent studies on the effect of alkoxides on the polymerization of styrene by alkyllithium reagents, we observed similar results.[15] The poly(styryllithium) solutions during the course of several hours at room temperature would decompose, going from yellow to colorless (higher concentrations went from red to brown to colorless). In both cases the solution became inactive, unable to react with styrene. Here we report the results from our studies on the reaction of poly(styryllithium) with THF.

Results

Poly(styryllithium) solutions (DP $\approx$ 20) that went colorless in THF were allowed to react with *tert*-butyldimethylsilyl chloride. After the polymer was precipitated, the solution was found to contain *tert*-butyldimethylsilylenolate, suggesting that the poly(styryllithium) cleaves THF in the same manner as ethyl- and butyllithium do. In order to verify this, we analyzed for ethylene by GC/MS in the reaction head space and found no significant amount of ethylene.

In order to evaluate the reaction products by GC/MS techniques, living oligomeric poly(styryllithium) (DP $\approx$ 3) was prepared in cold THF. A control sample was prepared by quenching the cold solution with ethanol. Analysis of the ethanol-quenched solution by GC/MS revealed the oligomers and their various isomers up to n = 5.[16] An identical solution was allowed to sit at room temperature until the solution went colorless. The solution was then quenched with ethanol. Analysis of this solution revealed products as above, as well as products with slightly longer retention times. These new peaks corresponded to the same oligomers as above plus one ethylene unit. Surprisingly, we were unable to find any addition product (1; R = Ps) that corresponded to the addition of poly(styryllithium) to THF (eq 1).[17]

Solutions of oligomeric poly(styryllithium) in THF were sparged with ethylene at room temperature. Upon quenching with ethanol nearly all of the oligomers were found to be converted to the corresponding oligomer with the addition of one or two ethylene units.

Lithium *n*- and *tert*-butoxide were added to solutions of poly(styryllithium) in the THF. The solutions of poly(styryllithium) were observed to darken from orange to a red–brown upon the addition of lithium *n*-butoxide, but the addition of lithium *tert*-butoxide had little if any effect on the color. The ^{1}H NMR spectra in THF-d_8 at −80 °C indicate that there is an interaction between the living end and the lithium *n*-butoxide. The ^{1}H NMR signals

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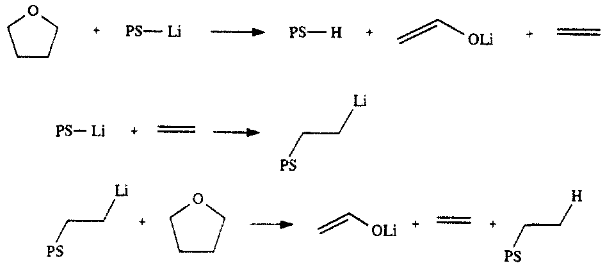
Scheme I



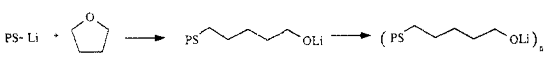
attributed to the benzyl group of the living end are shifted on the addition of lithium *n*-butoxide.[18]

Discussion

These results indicate that poly(styryllithium) is undergoing two reactions. First the poly(styryllithium) cleaves THF in the same manner as observed for *n*-butyllithium, and second the poly(styryllithium) adds to the ethylene produced from the cleavage of the THF, (Scheme I).

The NMR and visible spectra clearly show an interaction between lithium *n*-butoxide and poly(styryllithium). A similar interaction is expected for lithium enolate and poly(styryllithium). The reaction of poly(styryllithium) with THF produces lithium enolate, which may affect any synthetic or mechanistic studies. Several researches have carried out polymerization and propagation studies in THF with lithium counterions and have reported several oddities. It has been reported that the reactivity of the solution changes with time although the solution remains active, and in order to avoid this problem, poly(styryllithium) solutions in THF must by "freshly prepared".[8] It has also been noted that the solution darkens from red to brown on standing while the viscosity of the solution increases.[19]

Szwarc had noted previously that the viscosity of the poly(styryllithium)/THF solution increases on standing, indicating that the molecular weight was increasing. This was first attributed to slow association of the living polymer, going from ion pairs to covalent C–Li bonds or alternatively from ion pairs to ate complexes.[19] The color change on standing was offered as further evidence of this, with the darker color arising from the more associated species. An alternative explanation of this phenomenon was proposed by Fetters; the poly(styryllithium) adds to THF, and the resulting lithium alkoxide forms aggregates in THF, increasing the effective molecular weight and viscosity of the solution (eq 2).[20]



(2)

There are several examples of lithium alkoxides mixing with organolithium compounds. Mixed aggregates between lithium alkoxides and alkyllithiums are known.[21,22] Lochmann has reported a frequency shift in the visible region upon the addition of alkoxides to 1-lithio-1,1-diphenylhexane.[23] Further evidence of the cross-association of the living end with alkoxides is given by their effect on the rate of propagation.[15] This led us to conclude that mixed aggregates are forming between the living end and the resulting lithium enolate.

The addition of organolithium reagents to ethylene is known and has been reported several times. In order for the reaction to occur, the presence of basic solvents is required for the addition to proceed.[24] Even the addition of ethylene to substituted benzyllithiums has been reported.[25]

This observed change in the viscosity of the solution can be explained in several ways. There could be the formation of ate complexes such as $[PS_2Li_3(OCH{=}CH_2)_2]^-Li^+$. It is possible that the ethylene addition products, $(PSCH_2CH_2Li)_n$, being primary alkyllithiums, are aggregating to give dimers and tetramers. This would correspondingly raise the viscosity. We discount this since the half-lives of primary alkyllithiums in THF are fairly short at room temperature and they should be nearly colorless. We believe the best explanation of these observations is that the cleavage of THF gives rise to lithium enolate which cross-associates with poly(styryllithium). These mixed aggregates, such as $PS_2Li_4(OCH{=}CH_2)_2$, $PS_3Li_4(OCH{=}CH_2)$, and $PS_2Li_6(OCH{=}CH_2)_4$, are responsible for the increase in the viscosity.

The reaction of poly(styryllithium) with THF is an annoying side reaction affecting both the rate of propagation and the DP. This can largely be avoided by working at −60 °C. At this temperature very little decomposition occurs over the course of several hours.

Experimental Section

The THF and styrene were obtained from Aldrich Chemical Co. The THF was distilled from potassium/4-benzoylbiphenyl under nitrogen. The styrene was vacuum distilled from $LiAlH_4$ and kept at −60 °C under N_2 until use. The alkyllithium initiators and *tert*-butyldimethylsilyl chloride were obtained from the Lithium Division of FMC. The lithium *tert*-butoxide (Alfa) was sublimed before use. The lithium *n*-butoxide was prepared from *n*-butyllithium and *n*-butanol. ^1H NMR spectra were run in THF-d_8 (Cambridge) and obtained on a QE300 NMR spectrometer operating at 300.2 MHz.

All GC/MS data were obtained using HP 5890II gas chromatograph equipped with a HP 5971 series mass selective detector and a 25 m × 0.2 mm methylsilicone capillary column.

Preparation of Poly(styryllithium) (DP ≈ 3). A flame-dried flask was assembled in a glovebox. It was taken from the glove box, kept under a positive argon atmosphere, charged with 30 mL of THF, and cooled to −80 °C. *sec*-Butyllithium (3.5 mL, 1.3 M solution in hexane) and styrene (1.5 mL) were added sequentially via syringe to the cooled THF. The solution turned red. This solution was used for all of the reactions described below. Some of this solution was quenched with degassed ethanol at −80 °C. The majority of the products (low molecular weight oligomers) present could be identified using a GC/MS. These oligomers (**2**) were determined to be of the form $[CH_3CH_2(CH_3)CH(CH_2CHPh)_nH]$ (n = 1–3), from the mass spectra. A similar procedure was used for the preparation of living polystyrene, DP ≈ 20, except that 10 mL of styrene was used.

MS data (EI); *m/e* (relative intensity): Compound **2**, n = 1: 162 (21), 105 (9), 93 (8), 92 (100), 91 (58). Compound **2**, n = 2: 266 (23), 162 (15), 161 (5), 119 (5), 117 (20), 105 (29), 104 (13), 92 (25), 91 (100). Compound **2**, n = 3: 370 (10), 207 (11), 196 (20), 162 (23), 131 (10), 117 (26), 105 (27), 104 (23), 92 (21), 91 (100).

Reaction with THF. An aliquot of the above solution was allowed to warm to room temperature. After the solution went colorless (approximately 4 h), a solution of *tert*-butyldimethylsilyl chloride in THF was added. Examination of the solution revealed the oligomers as above, *tert*-butyldimethylsilylenolate (**3**), and a series of peaks with slightly longer retention times than the oligomers, the ethylene addition products, **4**, of the form ($[CH_3CH_2(CH_3)CH(CH_2CHPh)_n(CH_2CH_2)_mH]$; n = 1–3, m = 1).

MS data (EI); *m/e* (relative intensity): Compound **3**: 158 (3), 143 (2), 103 (11), 102 (11), 101 (100), 75 (12), 73 (9), 71 (7), 59 (36), 47 (6), 45 (13), 43 (6), 41 (8). Compound **4**, n = 1, m = 1: 190 (12), 161 (12), 120 (24), 119 (34), 105 (22), 92 (8), 91 (100). Compound **4**, n = 2, m = 1: 294 (15), 162 (28), 120 (41), 119 (42), 105 (26), 105 (15), 92 (12), 91 (100). Compound **4**, n = 3, m = 1: 398 (8), 224 (12), 207 (30), 162 (24), 120 (25), 119 (47), 105 (29), 104 (33), 91 (100).

Reaction with Ethylene. A portion of the above solution was sparged with ethylene at −80 °C. No change in the solution was observed. Upon warming to room temperature the red color rapidly disappeared. The reaction mixture was quenched with ethanol. The solution was then evaluated by GC/MS. This revealed that there were more ethylene addition products than above and more than one ethylene could be added, giving products as in **4** above but with m = 1–2.

MS data (EI); *m/e* (relative intensity): Compound **4**, n = 1, m = 2: 218 (8), 161 (12), 148 (17), 147 (20), 119 (7), 105 (28), 104 (7), 92 (10), 91 (100). Compound **4**, n = 2, m = 2: 322 (5), 209 (12), 208 (18), 207 (81), 162 (22), 148 (23), 147 (17), 134 (19), 105 (42), 104 (21), 92 (15), 91 (100).

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(4) Although generally less aggregated alkyllithiums are more reactive, there are exceptions. See: Kammermeir, B. O. T.; Klumpp, G. W.; Kolthof, K.; Vos, M. *Tetrahedron Lett.* **1991**, *32*, 3114.

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(16) At very long retention times tetramers and pentamers were observed. Only the monomers, dimers, and trimers were used to follow the reaction.

(17) Using GC/MS, we were able to observe the products reported by Bates[14] from the reaction of n-butyllithium with THF, but no addition product (n-octanol) was detected.

(18) ^{1}H NMR of the living end of poly(styryllithium): δ 5.17 (t, 1H), 5.29 (m, 2H), 5.73 (d, 1H), 5.92 (m, 2H). ^{1}H NMR of the living end of poly(styryllithium) in the presence of n-BuOLi: δ 5.13 (t, 1H), 5.23 (m, 2H), 5.69 (d, 1H), 5.87 (m, 2H).

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