

Why is Alkylation of an Enolate Accompanied by so Much Polyalkylation?

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Supporting Information

Alkylation of α -Tetralone with Benzyl Bromide. A preparative scale experiment was run by treating 0.93 g of α -tetralone in 14.7 g of THF with one equivalent of a solution of butyllithium in hexane. Two equivalents of benzyl bromide were added and stirred at room temperature. After 3 minutes an aliquot was quenched with isopropanol followed by water and extraction with methylene chloride. GC showed (without response corrections) a mono-/dialkylation ratio of 1.2/1. NMR analysis gave 90% α -tetralone and a mono-/di- ratio of 1.8. After complete reaction GC integration showed a di-/mono- ratio of >40/1.

2-Benzyl-6-phenyl- α -tetralone (2).¹ A mixture of 0.50 g (2.27 mmol) of 6-phenyl-1-tetralone and 4.5 mL of methyl magnesium carbonate (2.0 M in DMF) in 20 mL of anhydrous DMF was heated under argon at 120-130 °C for 1 h, 0.5 mL (2.9 mmol) of benzyl bromide was added to the cooled solution and kept on the steam bath for 6 h. Flash column chromatography and sublimation gave 0.30 g (42%) a white solid, mp 113-4 °C; NMR (300 MHz, CDCl₃): 1.83 (m, 1H), 2.14 (m, 1H), 2.63-2.83 (m, 2H), 3.01 (m, 2H), 3.50 (dd, 1H), 7.2-7.6 (m, 12H), 8.13 (d, 1H); MS (m/z), 312 (M⁺), 284, 221, 165, 91; Anal: Calc. for C₂₃H₂₀O, C, 88.42; H, 6.45; Found: C, 88.24; H, 6.44.

2,2-Dibenzyl-6-phenyl- α -tetralone (3). To a mixture of 2 and 1.1 equiv. of LDA in THF was added 2 equiv. of benzyl bromide. Flash column chromatography and recrystallization from ether/pentane gave a white solid, mp 145-6 °C; NMR

(300 MHz, CDCl₃) 8.16 (d, 1H), 7.60-7.14 (m, 17H), 3.35 (d, 2H), 3.10 (t, 2H), 2.67 (d, 2H), 1.96 (t, 2H); Anal: Calc. for C₃₀H₂₆O, C, 89.51, H, 6.51; found: C, 89.49, H, 6.43.

Table S1. Typical Lambert-Beers Law run (Run 818) for **1-Li**.(1 mm cell)

{LiPAT}, M	λ_{max} , nm	Abs(λ_{max})/0.1	Abs(367nm)/0.1
0.0014350	337.5	16.521	8.5890
0.0012040	338.0	13.712	7.2290
0.00096690	337.5	10.978	5.8340
0.00084190	338.0	9.517	5.0480
0.00074960	337.5	8.467	4.5030
0.00067440	337.0	7.613	4.0660
0.00060390	337.5	6.818	3.6580
0.00054800	337.5	6.152	3.2880
0.00049890	337.0	5.604	2.9960
0.00046040	337.5	5.144	2.7770
0.00041550	337.5	4.661	2.5070
0.00038570	338.0	4.309	2.3260
0.00036010	337.5	4.032	2.1860
0.00033600	337.5	3.766	2.0340
0.00031120	338.0	3.484	1.8880
0.00028500	338.0	3.200	1.7300
0.00025350	336.5	2.826	1.5500
0.00021740	337.0	2.412	1.3180
0.00018600	337.5	2.056	1.1200
0.00016440	338.5	1.842	1.0170
0.00012860	338.5	1.436	0.7840

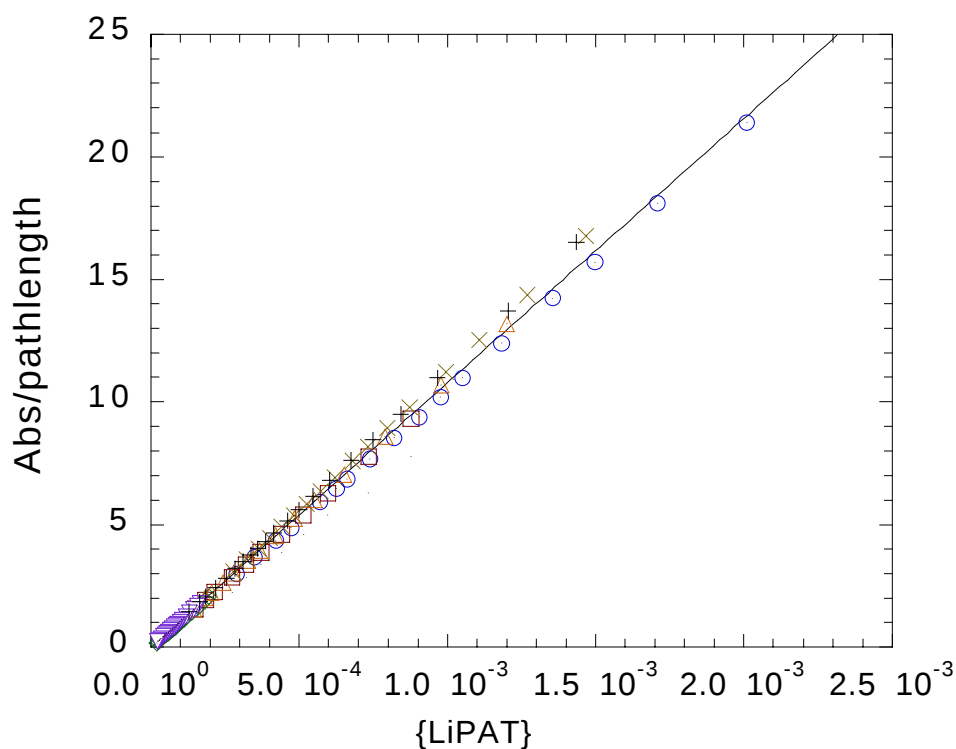


Fig. S1. Plot of absorbance in THF at 25 °C at λ_{max} vs {LiPAT}, the formal concentration of **1-Li** for seven runs; the slope of the line shown is 10784 ± 57 , $R^2 = 0.993$.

Table S2. Spectral data for LiBnPAT in THF at 25 °C.

{LiBnPAT} (M)	λ_{max} (nm)	Absorbance at 361.0 nm	Absorbance at λ_{max}
Series 1	1 mm cell		
0.001687	359.5	2.1985	2.2039
0.0013755	359	1.7604	1.7692
0.0011921	359.5	1.5219	1.5225
0.0010348	360	1.315	1.3159
0.0009123	360.5	1.1568	1.1571
0.0008136	361	1.0279	1.0279
0.0007051	362	0.8886	0.889
0.0006183	363	0.7745	0.7757
0.0005412	359.5	0.6763	0.6766
0.0004741	362	0.5893	0.5896
0.0004132	363	0.512	0.5135
0.0003607	361.5	0.4507	0.4507
Series 2	1 cm cell		
0.0001373	362.5	1.689	1.6912
0.0001262	362.5	1.574	1.5794
0.0001081	362.5	1.314	1.3208

0.0001015	362.5	1.232	1.2398
0.0000867	362.5	1.044	1.0509

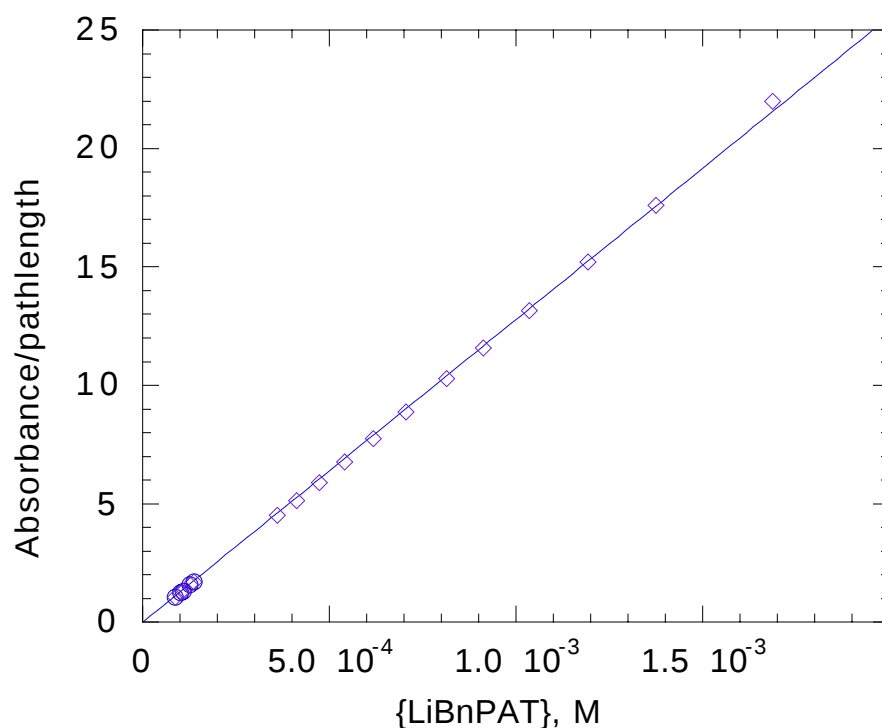


Fig. S2. Plot of absorbance in THF at 25 °C for 1 cm cell vs {LiBnPAT}, the formal concentration of **2-Li** for two runs; the slope of the line shown is 12779 ± 46 , $R^2 = 0.999$.

Table S3. Ion pair acidity experiments with LiPAT and either Ph₃,4-BF

{LiPAT}, M	{LiPh ₃ 4BF}, M	[PAT], M	[Ph-3,4-BF] M	Kcorr	pK _{ob}	{LiPAT}/Kcorr
Run 1						
1.71E-04	5.95E-05	5.12E-03	7.44E-03	6.288	14.08	2.72E-05
1.94E-04	6.55E-05	5.10E-03	7.43E-03	6.365	14.08	3.05E-05
4.27E-04	9.04E-05	4.86E-03	7.41E-03	10.01	13.88	4.26E-05
6.05E-04	1.06E-04	4.69E-03	7.39E-03	12.25	13.79	4.94E-05
8.33E-04	1.20E-04	4.46E-03	7.38E-03	15.33	13.69	5.44E-05
1.37E-03	1.53E-04	3.92E-03	7.34E-03	21.67	13.54	6.33E-05
1.62E-03	1.67E-04	3.67E-03	7.33E-03	24.74	13.49	6.55E-05
Run 2						
1.18E-04	7.98E-05	3.31E-03	7.29E-03	4.624	14.21	2.55E-05
1.75E-04	9.42E-05	3.25E-03	7.28E-03	5.735	14.12	3.05E-05
2.17E-04	1.04E-04	3.21E-03	7.27E-03	6.422	14.07	3.39E-05
2.77E-04	1.15E-04	3.15E-03	7.26E-03	7.396	14.01	3.74E-05
3.49E-04	1.26E-04	3.08E-03	7.25E-03	8.618	13.94	4.04E-05
4.10E-04	1.37E-04	3.02E-03	7.24E-03	9.367	13.91	4.38E-05
4.72E-04	1.47E-04	2.96E-03	7.23E-03	10.17	13.87	4.64E-05

5.46E-04	1.57E-04	2.88E-03	7.22E-03	11.22	13.83	4.87E-05
6.07E-04	1.65E-04	2.82E-03	7.21E-03	12.04	13.8	5.05E-05
6.63E-04	1.73E-04	2.77E-03	7.20E-03	12.73	13.78	5.21E-05
7.33E-04	1.81E-04	2.70E-03	7.19E-03	13.66	13.74	5.37E-05
8.18E-04	1.94E-04	2.61E-03	7.18E-03	14.55	13.72	5.62E-05
8.60E-04	1.98E-04	2.57E-03	7.17E-03	15.19	13.7	5.66E-05
Run 3						
5.50E-05	3.39E-05	4.37E-03	7.41E-03	4.713	14.21	1.17E-05
9.56E-05	5.04E-05	4.33E-03	7.39E-03	5.036	14.18	1.90E-05
1.39E-04	6.20E-05	4.29E-03	7.38E-03	5.77	14.12	2.41E-05
1.96E-04	7.29E-05	4.23E-03	7.37E-03	6.75	14.05	2.90E-05
2.57E-04	8.29E-05	4.17E-03	7.36E-03	7.729	13.99	3.32E-05
3.15E-04	9.10E-05	4.11E-03	7.35E-03	8.616	13.94	3.66E-05
3.70E-04	1.00E-04	4.05E-03	7.34E-03	9.158	13.92	4.05E-05
4.60E-04	1.09E-04	3.96E-03	7.33E-03	10.59	13.86	4.34E-05
5.44E-04	1.16E-04	3.88E-03	7.33E-03	11.84	13.81	4.60E-05
6.69E-04	1.26E-04	3.76E-03	7.32E-03	13.68	13.74	4.89E-05
7.86E-04	1.36E-04	3.64E-03	7.31E-03	15.21	13.7	5.17E-05
8.94E-04	1.45E-04	3.53E-03	7.30E-03	16.54	13.66	5.41E-05
Run 4						
{LiPAT}, M ^a	{LiTPI}, M	[PAT], M	[TPI], M	Kcorr	pK _{ob}	{LiPAT}/Kcorr
5.44E-05	3.09E-05	4.59E-03	7.05E-03	4.746	14.29	1.15E-05
1.05E-04	5.06E-05	4.54E-03	7.03E-03	5.003	14.27	2.11E-05
1.54E-04	5.96E-05	4.49E-03	7.02E-03	6.048	14.19	2.54E-05
2.16E-04	6.99E-05	4.43E-03	7.01E-03	7.111	14.12	3.03E-05
3.25E-04	8.02E-05	4.32E-03	7.00E-03	9.312	14	3.49E-05
4.29E-04	8.78E-05	4.22E-03	6.99E-03	11.31	13.92	3.79E-05
5.33E-04	9.76E-05	4.11E-03	6.98E-03	12.75	13.86	4.18E-05
6.76E-04	1.06E-04	3.97E-03	6.97E-03	15.13	13.79	4.47E-05
8.15E-04	1.17E-04	3.83E-03	6.96E-03	16.86	13.74	4.83E-05
9.77E-04	1.30E-04	3.67E-03	6.95E-03	18.68	13.7	5.23E-05
1.13E-03	1.41E-04	3.52E-03	6.94E-03	20.57	13.66	5.47E-05

(a) Neutral TPI has strong absorption below 360.0 nm, therefore, the abso 6340) was used to obtain the concentration of {LiPAT}.

Table S4. Ion pair acidity experiments with LiBnPAT (2a) and TeFPFl.

{LiBnPAT}, M	{LiTeFPFl}, M	[BnPAT], M	[TeFPFl] M	Kcorr	pK _{ob}	{LiBnPAT}/Kcorr
8.44E-04	6.50E-04	4.12E-03	1.90E-02	5.54	13.377	1.53E-04
6.43E-04	5.26E-04	4.37E-03	1.92E-02	5.02	13.419	1.28E-04
6.31E-04	5.13E-04	4.39E-03	1.92E-02	5.03	13.419	1.25E-04
6.09E-04	4.99E-04	4.41E-03	1.92E-02	4.98	13.423	1.22E-04
3.25E-04	3.29E-04	3.88E-03	1.60E-02	3.87	13.532	8.39E-05
2.62E-04	2.75E-04	3.97E-03	1.61E-02	3.69	13.553	7.10E-05
1.42E-04	1.79E-04	3.14E-03	1.25E-02	3.02	13.641	4.70E-05
1.30E-04	1.67E-04	3.16E-03	1.25E-02	2.97	13.648	4.38E-05
1.46E-03	3.84E-04	1.94E-03	4.07E-03	7.25	13.260	2.02E-04
1.10E-03	3.12E-04	1.74E-03	3.39E-03	6.27	13.323	1.75E-04
1.01E-03	2.91E-04	1.83E-03	3.42E-03	5.97	13.344	1.69E-04
9.82E-04	2.82E-04	1.86E-03	3.42E-03	5.91	13.348	1.66E-04
9.71E-04	2.82E-04	1.87E-03	3.42E-03	5.82	13.355	1.67E-04

Table S5. Initial rates of reaction of **1-Li** with benzyl bromide at 25 °C in THF; [BnBr] = 0.02073M.

{ 1-Li }, M	rate, M s ⁻¹	[M], M	[T], M
4.13E-04	3.80E-07	1.86E-04	5.67E-05
6.42E-04	4.15E-07	2.18E-04	1.06E-04
8.15E-04	4.61E-07	2.36E-04	1.46E-04
1.10E-03	5.09E-07	2.59E-04	2.11E-04
2.03E-04	3.07E-07	1.37E-04	1.66E-05
4.94E-04	3.92E-07	1.99E-04	7.37E-05
7.46E-04	4.38E-07	2.29E-04	1.27E-04
9.65E-04	4.97E-07	2.49E-04	1.79E-04
1.19E-03	4.86E-07	2.65E-04	2.32E-04
1.76E-03	5.89E-07	2.97E-04	3.66E-04
1.31E-03	5.26E-07	2.72E-04	2.57E-04
4.07E-04	3.86E-07	1.86E-04	5.56E-05
7.36E-04	4.32E-07	2.28E-04	1.27E-04

Table S6. Initial rates of reaction of **2-Li** with benzyl bromide at 25 °C in THF; [BnBr] = 0.01542M.

{ 2-Li }, M	rate, M s ⁻¹	[M], M	[D], M
1.42E-03	1.03E-06	3.72E-04	5.25E-04
9.49E-04	8.52E-07	2.94E-04	3.27E-04
1.26E-03	8.45E-07	3.47E-04	4.57E-04
3.34E-04	4.00E-07	1.54E-04	9.02E-05
7.12E-04	6.73E-07	2.47E-04	2.32E-04
1.12E-03	8.46E-07	3.24E-04	3.99E-04
5.75E-04	5.93E-07	2.17E-04	1.79E-04
5.01E-04	5.08E-07	1.99E-04	1.51E-04
9.92E-04	8.27E-07	3.01E-04	3.45E-04

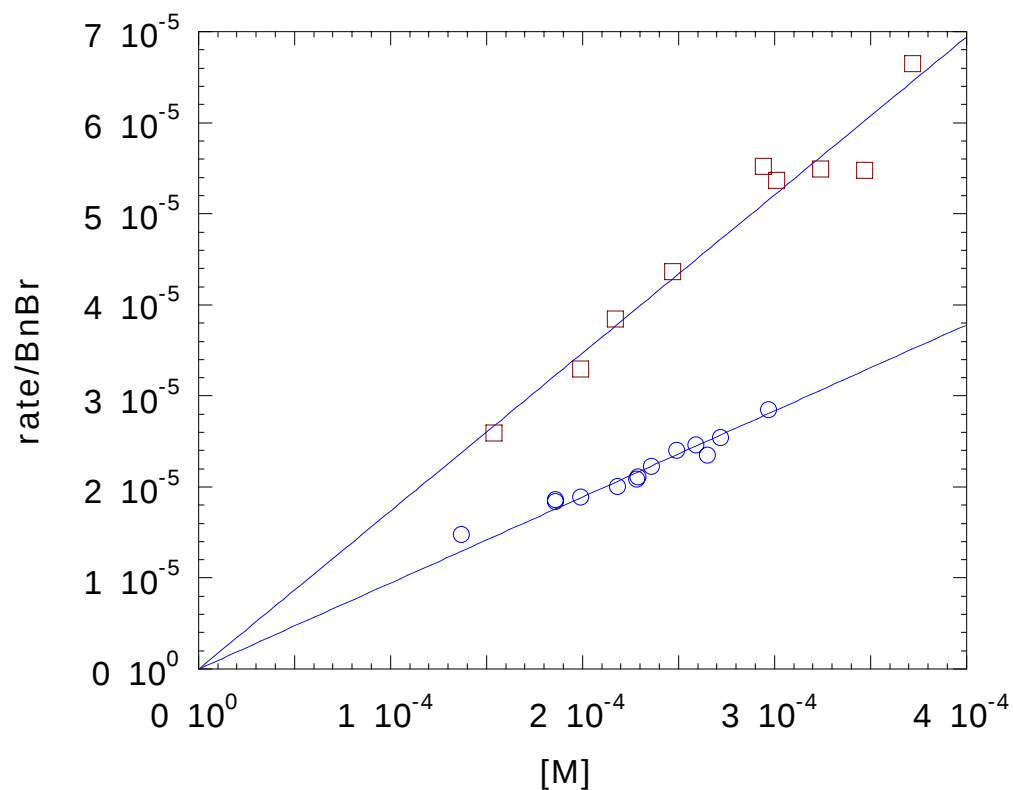


Figure S3. Plots of rate/[BnBr] for reactions of **1-Li** (circles) and **2-Li** (squares) vs monomer concentration. Slopes of lines through the origin are 0.0945 ± 0.0010 and 0.174 ± 0.003 , respectively.

¹ Preparation by Kai-Cha Feng.