then maintained at this temperature for 2.5 h. The dark amber mixture was dumped onto 300 mL of crushed ice. The pH was adjusted to 8 using a 4 M NaOAc solution. A light green precipitate formed during and after this addition. After stirring at room temperature for 24 h, the solid was collected by vacuum filtration. Recrystallization (EtOAc/hexanes) of the crude solid yielded 0.86 g (75%) of a dull gold solid, **6c**, mp 194–195 °C: IR (KBr) 1685, 1645 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 10.62 (s, 1 H), 8.5 (dd, J = 0.75, 8.16 Hz, 1 H), 7.84–7.81 (m, 2 H), 7.64–7.61 (m, 1 H), 7.52 (d, J = 4.16 Hz, 1 H), 6.86 (d, J = 4.16 Hz, 1 H); ^{13}C NMR (DMSO-d_6) δ 180.9, 159.3, 135.4, 134.0, 133.2, 130.8, 128.6, 127.0, 125.8, 121.6, 121.5, 109.6; MS [m/z (relative intensity)] 229 (M$^+$, 100), 201 (34.3), 172 (45.6). Anal. Calcd for $C_{12}H_7NO_2S$: C, 62.87; H, 3.08; N, 6.11. Found: C, 62.81; H, 3.21; N, 6.17.

Nitration of 6a: 3-Nitropyrrolo[2,1-*b*][1,3]benzothiazin-9-one (6e) and 1-Nitropyrrolo[2,1-*b*][1,3]benzothiazin-9-one (6f). To a stirred solution of **6a** (0.75 g, 3.7 mmol) in acetic anhydride (40 mL) at 0 °C was added a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.03 g, 4.25 mmol, 1.15 equiv) in acetic anhydride (60 mL) dropwise over 10 min. After stirring for 2.5 h on an ice bath, the dark mixture was poured slowly into 200 mL of a 5% $NaHCO_3$ solution and stirred for 30 min. The brown solid that formed was collected by vacuum filtration and dried overnight. The brown solid (0.70 g) was extracted for 3 h with $CHCl_3$ in a Soxhlet extractor and the obtained extract was concentrated to about 5 mL in vacuo and chromatographed (1:1 $CHCl_3$/hexanes). Four bands were obtained: the first (highest R_f) was starting material **6a**, 0.09 g. The next band (0.01 g) contained only the 3-isomer **6e**. The third band (0.04 g) contained a mixture of **6e** and **6f**, while the fourth (0.53 g) contained **6e**, **6f**, and impurities. Preparative TLC (1:1 $CHCl_3$/hexanes) was performed on the fourth band but only the 3-nitro isomer was isolated (trace amount).

3-Nitropyrrolo[2,1-*b*][1,3]benzothiazin-9-one (6e): ^{1}H NMR δ 8.62 (dd, J = 1.51, 8.0 Hz, 1 H), 7.93 (d, J = 3.84 Hz, 1 H), 7.78–7.46 (m, 3 H), 7.18 (d, J = 3.84 Hz, 1 H).

1-Nitropyrrolo[2,1-*b*][1,3]benzothiazin-9-one (6f) (inferred from a mixture of the 1- and 3-isomers): ^{1}H NMR δ 8.48 (dd, J = 1.33, 7.9 Hz, 1 H), 7.78–7.46 (m, 3 H), 7.42 (d, J = 4.19 Hz, 1 H), 6.39 (d, J = 4.19 Hz, 1 H).

Acknowledgment. We wish to thank Mr. Steve Hahn (Dow Chemical Co., Midland, MI) for NMR spectral data and Mr. R. T. Winters (Parke-Davis Pharmaceutical Research Institute, Ann Arbor, MI) for disclosing his success with the two-phase sodium *m*-periodate oxidation procedure. Appreciation is also expressed to the Graduate School of Michigan Tech University for fellowship support of K.A.T.

Preparation and Remarkable Reactivity of the Elusive (1,1,3,3-Tetramethylallyl)lithium

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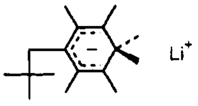
Although traditional methods of allyllithium production failed for (1,1,3,3-tetramethylallyl)lithium, it was readily prepared in a two-pot sequence starting with mesityl oxide. The key step is reductive lithiation of 4-(phenylthio)-2,4-dimethyl-2-pentene with lithium 1-(dimethylamino)naphthalenide. Treating the reductive lithiation product with trimethylstannyl chloride and the resulting allylstannane with methyllithium in the presence of *N,N,N,N*-tetramethylethylenediamine provided a solution of the allyllithium free of lithium thiophenoxide. This material adds to anthracene at −78 °C.

In our continuing investigations of structure and behavior of allyllithium–amine complexes, we developed a need for (1,1,3,3-tetramethylallyl)lithium, the simplest example of a highly alkylated conjugated carbanion salt. Most experimental evidence for carbanionic species in solution supports the conclusion that α-alkyl substituents destabilize carbanions.[2] Whether such effects apply to peralkylated π-conjugated carbanions is less clear since there are relatively few examples of such species. Further, other interactions intrude. For example, the unexpected stability of the (peralkylcyclohexadienyl)lithium salt 1 was correctly ascribed to steric inhibition to aromatization.[3]



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In this paper, we reveal the difficulties encountered in the traditional methods of generating (1,1,3,3-tetramethylallyl)lithium, a highly efficient process for its preparation based on reductive lithiation of an allyl phenyl thioether, and an observation concerning its surprising reactivity towards anthracene.

Results and Discussion

The traditional routes to allyllithiums such as ether cleavage[4] or metal reduction of the appropriate halide[5] do not result in (1,1,3,3-tetramethylallyl)lithium[6] and do not provide intermediates which could be used to prepare tin compounds, the best precursors of allyllithiums.[7] For

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[1] (a) Ohio State University. (b) University of Pittsburgh.

[2] See, for example: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Vol. 2, pp 405–416.

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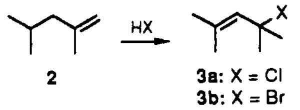
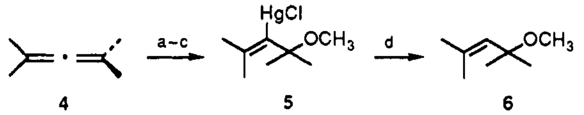
0022-3263/92/1957-3680$03.00/0

example, we confirm the reports of Russian workers who prepared 1,1,3,3-tetramethylallyl chloride (**3a**) and the corresponding bromide (**3b**) by passing the appropriate gaseous hydrogen halide into 2,4-dimethyl-1,3-pentadiene but failed to convert these halides into Grignard reagents.[6] We find that these halides can be washed with aqueous $NaHCO_3$ and give acceptable NMR spectra but are always contaminated with hydrogen halide. Then, ether **6** was prepared by methoxy mercuration of tetramethylallene (**4**) followed by borohydride reduction of mercuri intermediate **5**. All attempts to cleave ether **6** with metals–K in pentane or Li in diethyl ether or THF–resulted in elimination of metal alkoxide with formation of diene **2**.

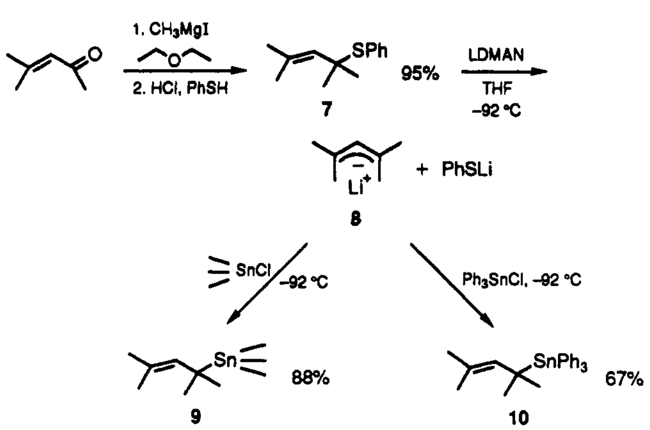


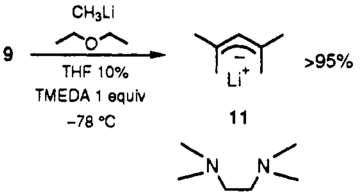


$$6 \xrightarrow[\text{pentane}]{\text{K}} 2 + CH_3OK$$

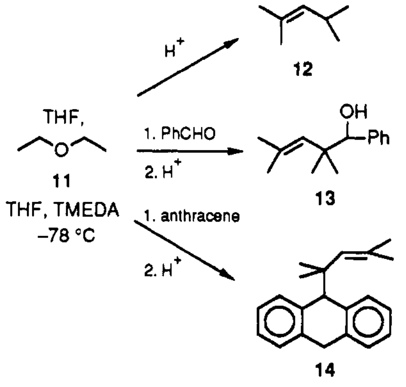
In recent years, it has been amply demonstrated that aromatic radical-anion induced reductive lithiation[7-9] of allyl phenyl thioethers is a versatile and general method of generation of allyllithiums.[10] It has been pointed out[9] that two very attractive features of reductive lithiation of phenyl thioethers as a method for the production of organolithiums are the great ease of preparation of the substrates and the fact that the more highly substituted, and thus less stable, organolithiums are more easily produced than the less highly substituted ones. Both of these features are now strikingly demonstrated by the two-pot generation of (1,1,3,3-tetramethylallyl)lithium (**8**) starting from inexpensive mesityl oxide. Addition of methylmagnesium iodide to the latter followed by thiophenol/HCl yields the substrate **7** in excellent yield. Reductive lithiation with lithium 1-(dimethylamino)naphthalenide (LDMAN)[10] in THF at -92 °C resulted in a yellow solution assumed to contain (1,1,3,3-tetramethylallyl)lithium (**8**). Quenching **8**, separately, with trimethyltin chloride and triphenyltin chloride yielded the desired tin compounds **9** and **10**, respectively.

In attempts to prepare pure samples of (1,1,3,3-tetramethylallyl)lithium for subsequent study, the triphenylstannyl derivative **10** was treated with *n*-butyllithium in diethyl ether–TMEDA at room temperature. Only small amounts of phenyllithium could be detected by NMR but no sign of the desired (tetramethylallyl)lithium. Reacting **10** under the same conditions with phenyllithium gave 20% of hydrolysate, 2,4-dimethyl-2-pentene, and the rest starting material, implying that some of the desired allylic lithium compound had formed. Finally, we found that reaction of the trimethylstannyl derivative **9** with methyllithium in diethyl ether–THF–TMEDA at -78 °C gave almost quantitative conversion, >95%, to the desired allyllithium **11**, an orange solution. This is indicated by its ^{13}C NMR spectrum (C_1 and C_3 59.72, C_2 138.28, CH_3 25.85, all δ units) as well as its expected products on hydrolysis, **12**, and with benzaldehyde, **13**.





In addition to the above electrophiles, **11** appears to react with aromatic molecules. From the original reduction of sulfide **7** by lithium (dimethylamino)naphthalenide, there was obtained small amounts of a reduced naphthalene. Accordingly, **11** was exposed to anthracene in diethyl ether–THF–TMEDA at -78 °C. Within minutes, the orange color due to **11** turned deep red, indicating the presence of the 9,10-dihydroanthryl anion. Hydrolysis of this reaction mixture gave 9-(1,1,3-trimethyl-2-butenyl)-9,10-dihydroanthracene (**14**) as determined from its NMR and mass spectra. In particular, NMR shows the allylic substituent to be axial as observed for 9-substituted 9,10-dihydroanthracenes previously.[12]



At -78 °C, we find that several organolithium compounds are unreactive to anthracene under the following conditions: *tert*-butyllithium in pentane with 1 equiv of TMEDA;[13] *tert*-butyllithium in THF; *tert*-butyllithium with 1 equiv of TMEDA and 10% THF in diethyl ether; *n*-butyllithium with 1 equiv of TMEDA and 10% THF in

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diethyl ether. All these experiments, after quenching with CH_3OD, yielded unchanged anthracene. Compared to all known addition reactions of organolithium compounds to arenes (not heteroarenes), both photochemical and thermal, compound 11 is the most reactive one reported so far. In general, such reactions take place using RLi complexes with THF or tertiary amines between 20 °C and 80 °C.[14] In one case, *n*-butyllithium was reported to add to anthracene in THF at -30 °C to -40 °C.[14g] Polymer-substituted allyllithium is also unreactive to anthracene. Thus, live end allylic lithium produced by *n*-butyllithium initiated polymerization of 1,3-butadiene does not react with anthracene at room temperature in hexane–TMEDA.[15] Simple alkyllithiums add to anthracene photochemically (medium pressure mercury lamp) in ethers at 25 °C.[16] In hydrocarbon media, addition of alkyllithiums (*tert*-butyl, 2-butyl, and *n*-butyl) requires temperatures of ca. 168 °C.[17]

In summary, we have demonstrated the utility of reductive cleavage of phenyl sulfides to produce the highly substituted and unstable (1,1,3,3-tetramethylallyl)lithium (11). Collectively, the above results show that 11 is significantly more reactive than other organolithium compounds. The origin of this reactivity is not now clear.

Experimental Section

Attempted Generation of Grignard Reagents from 2,4-Dimethyl-4-chloro-2-pentene (3a) and 2,4-Dimethyl-4-bromo-2-pentene (3b). The above halides were generated by reactions of the appropriate hydrogen halide with neat 2,4-dimethyl-2,4-pentadiene at -20 °C. Crude products in diethyl ether were washed with aqueous Na_2CO_3 and then dried with $MgSO_4$. The samples of halides, on initial isolation, were 99% pure yet always contained some acid. All attempts to react these compounds with Mg (sublimed) in diethyl ether or THF failed to result in Grignard reagents, rather 2,4-dimethyl-1,3-pentadiene and unidentified polymeric products were found.

Attempted Preparation of (1,1,3,3-Tetramethylallyl)potassium. At room temperature 1,1,3,3-tetramethylallyl methyl ether (6) (1.8 g, 0.014 mol) was treated with potassium chips (0.7 g, 0.018 mol) over a period of 2 h. The reaction mixture was treated with trimethylchlorosilane (1.5 g, 0.014 mol). Normal workup revealed by gas chromatographic analysis 91% starting material and 9% 2,4-dimethyl-2-pentene.

In a second experiment the methyl ether (3.6 g, 0.028 mol) was treated with 1 mL of sodium–potassium alloy (1:1 by weight) in 10 mL of THF at -20 °C and the mixture was warmed slowly to 0 °C over 1 h. Hydrolysis resulted in 90% of 2,4-dimethyl-2,4-pentadiene and the rest 2,4-dimethyl-2-pentene, known compounds, as determined from gas chromatography and NMR data.

4-Methoxy-2,4-dimethyl-2-pentene (6). Tetramethylallene (42.9 g, 0.447 mol) was added to an equivalent quantity of mercuric acetate in 600 mL of anhydrous methanol at room temperature over a period of 20 min. The solution at first turned light green. With an additional 10 min of stirring the solution became colorless. The liberated acetic acid was then neutralized with 53 g of Na_2CO_3. Methanol was removed under reduced pressure and the remaining solid stirred with aqueous NaCl. White 3-(chloromercurio)-4-methoxy-2,4-dimethyl-2-pentene (5) precipitated out and was filtered and washed with aqueous NaCl. This compound was obtained in 85% yield (132 g). ^1H NMR ($CDCl_3$, ppm): aliphatic CH_3 1.37, allylic CH_3 1.9 and 2.0, methoxy 3.22. To this entire product in 250 mL of aqueous 3 N NaOH solution was added 250 mL more of 3 N NaOH followed by 40 g of $NaBH_4$. This mixture was stirred for an additional hour and then extracted with cyclohexane. The solvent was evaporated and 30 g of compound 6 was isolated by distillation, bp 123–124 °C, 1 Torr, in 61% yield. ^1H NMR ($CDCl_3$, ppm): aliphatic CH_3 1.12, allylic CH_3 1.7 and 1.79, methoxy 3.06, vinyl 5.06. MS: M^+ 97.

4-(Phenylthio)-2,4-dimethyl-2-pentene (7). A 1-L, three-necked flask fitted with an addition funnel and an argon inlet adaptor was charged by cannulation with 81.0 g of CH_3MgI (0.49 mol) in 400 mL of diethyl ether. The solution was cooled to an ice bath temperature and 14.7 g of mesityl oxide (0.15 mol) in 35 mL of diethyl ether was added dropwise over 2 h. After a total time of 3 h, bubbling of HCl gas directly into the solution with a syringe needle and dropwise addition of 16.5 g of thiophenol (0.15 mol) in 35 mL of diethyl ether were initiated simultaneously. The HCl gas was then removed halfway through the addition, about 0.5 h, and the solution was stirred 1 h more upon completion of the addition. The reaction was then quenched with 50 mL of 5% NaOH solution. The organic phase was extracted, washed five times with 50 mL of the hydroxide solution and once with brine, and then dried over $MgSO_4$. Concentrating under vacuum followed by distillation yielded 25.13 g (0.1218 mol, 95%) of 4-(phenylthio)-2,4-dimethyl-2-pentene (7), bp 67 °C, 0.15 Torr. ^1H NMR ($CDCl_3$, ppm): Ar 7.42–7.39 and 7.23–7.20 (m, 5 H), $(CH_3)_2C{=}C\mathit{H}$ 5.13 (m, 1 H), $={CHC(C\mathit{H}_3)_2}{-}$ 1.44 (s, 6 H), exo CH_3 1.711 (d, 3 H, $^4J(CH_3{-}CH) = 1.72$ Hz), endo CH_3 1.718 (d, 3 H, $^4J(CH_3{-}CH) = 1.55$ Hz). ^{13}C NMR: exo CH_3 27.77, endo CH_3 18.97, $(CH_3)_2\mathit{C}{=}$ 134.62, $(CH_3)_2C{=}\mathit{C}H{-}$ 133.53, $=CH\mathit{C}(CH_3)_2{-}$ 49.09, $=CHC(\mathit{C}H_3)_2$ 30.75, Ar 136.90, 128.22, 130.52, 128.09. MS: M^+ 206 ($C_{13}H_{18}S$, 2), 109 (C_6H_5S, 12), 97 (C_7H_{13} and C_5H_5S, 100), 55 (C_4H_7, 55).

4-(Trimethylstannyl)-2,4-dimethyl-2-pentene (9). A 250-mL Schlenk flask with a glass-coated stir bar was flamed and cooled under vacuum. Under a flow of argon, the flask was charged with 4.52 g (0.026 mol) of *N,N*-dimethyl-1-naphthalenamine and 25 mL of tetrahydrofuran. Some lithium slivers were then added to the solution at room temperature. Once formation of the radical anion ensued, as indicated by the dark green color, the reaction flask was immersed in an external bath at -45 to -55 °C. Lower temperatures suppressed formation of the radical anion. The remaining slivers of lithium were then added to bring the total to 0.026 mol, 1.05 molar equiv, and the reaction was allowed to proceed. After 5 h, the reaction flask was placed in a bath at -92 °C. A $^3/_4$ fraction of 2.72 g (0.0132 mol) of 7 in 10 mL of tetrahydrofuran was then added dropwise from an addition funnel over a period of 40 min. The remaining $^1/_4$ portion of 7 was mixed with 2.63 g (0.0132 mol) of trimethyltin chloride in 10 mL of tetrahydrofuran and the addition was continued dropwise at the same rate. The duration of the reaction was extended by 1 h upon addition of all reagents, after which it was quenched with 30 mL of 0.1 N NaOH. The aqueous phase was saturated with NaCl and the organic phase extracted, washed thrice with hydroxide solution, dried over $MgSO_4$, and then concentrated under low vacuum. The yield of 9 determined by gas chromatographic analysis of the crude reaction product was nearly quantitative, 95%. Compound 9 (3.05 g) was distilled directly from the crude mixture, bp 78 °C at 2 Torr, in 88% yield. ^1H NMR ($CDCl_3$, ppm): $(CH_3)_2C{=}C\mathit{H}{-}$ 5.205 (m, 1 H, $^3J(Sn{-}H) = 30.37$ Hz), $=CHC(C\mathit{H}_3)_2{-}$ 1.279 (6 H, $^3J(Sn{-}CH_3) = 67.60$ Hz and 64.7 Hz), exo CH_3 1.646 (d, 3 H, $^4J(CH_3CH) = 1.17$ Hz), endo CH_3 1.691 (d, 3 H, $^4J(CH_3{-}CH) = 1.14$ Hz), $Sn(C\mathit{H}_3)_3$ 0.019 (9 H, m, $^2J(Sn{-}H) = 47.62$ and 49.63 Hz). ^{13}C NMR exo CH_3 27.65, $(CH_3)_2\mathit{C}{=}$ 135.37, endo CH_3 19.43, $(CH_3)_2C{=}\mathit{C}H{-}$ 127.16, $=CH\mathit{C}(CH_3)_2$ 27.50, $=CHC(\mathit{C}H_3)_2$ 28.76, $Sn(\mathit{C}H_3)_3$ -10.05. MS: M^+ 260 ($C_{10}H_{22}Sn$, 3), 165 (C_3H_9Sn, 100), 135 (CH_3Sn, 24), 97 (C_7H_{13}, 34), 55 (C_4H_7, 26).

4-(Triphenylstannyl)-2,4-dimethyl-2-pentene (10). A 250-mL Schlenk flask with a glass-coated stir bar was flamed and cooled under vacuum. Under a flow of argon, the flask was charged with 4.52 g (0.026 mol) of *N,N*-dimethyl-1-naphthalenamine and 25 mL of tetrahydrofuran. Lithium slivers were then added to the solution at room temperature and once formation of the radical anion had ensued, the reaction flask was immersed

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in an external bath at −92 °C. The remaining lithium slivers were then added to bring the total to 0.026 mol, 1.05 molar equiv, and the reaction was allowed to proceed. After 8 h, a $^3/_4$ portion of 2.72 g (0.0132 mol) of **7** in 10 mL of tetrahydrofuran was added dropwise from an addition funnel over a period of 40 min. The remaining $^1/_4$ fraction of **7** was mixed with 5.08 g (0.0132 mol) of triphenyltin chloride in 30 mL of tetrahydrofuran and the addition was then continued dropwise. The reaction was allowed to continue for 1 h more upon addition of all reagents, at which time it was quenched with 0.1 N NaOH. The reaction mixture was purified by complete extraction of thiophenol with 0.2 N NaOH solution and extraction of *N,N*-dimethyl-1-naphthalenamine with 0.2 N HCl solution. Gas chromatographic analysis placed the reaction yield of **10** at 67%. Extraction of unreacted 4-(phenylthio)-2,4-dimethyl-2-pentene from the crude product dissolved in diethyl ether was accomplished by numerous washings with 0.015 M $AgNO_3$ in 15% aqueous ethanol. Crystallization of the product was effected with 2-propanol/pentane, mp 48–49 °C. ^1H NMR ($CDCl_3$, ppm): $(CH_3)_2C{=}C\mathit{H}{-}$ 5.406 (m, 1 H, $^3J(Sn{-}H) = 31.94$ Hz), $={CHC(C\mathit{H}_3)_2}{-}$ 1.279 (6 H, $^3J(Sn{-}CH_3) = 67.60$ and 64.7 Hz), exo CH_3 1.332 (d, 3 H, $^4J(CH_3{-}CH) = 1.02$ Hz), endo CH_3 1.616 (d, 3 H, $^4J(CH_3{-}CH) = 0.87$ Hz), Ar 7.50–7.47 and 7.29–7.27 (9 H, m, $^2J(Sn{-}H) = 47.62$ and 49.63 Hz). ^{13}C NMR exo CH_3 28.34, $(CH_3)_2\mathit{C}{=}$ 139.7, endo CH_3 19.78, $(CH_3)_2C{=}\mathit{C}H{-}$ 134.00, ${=}CH\mathit{C}(CH_3)_2{-}$ 35.45, ${=}CHC(\mathit{C}H_3)_2$ 30.05, Ar 137.5, 129.6, 129.3. MS: M^+ 448 ($C_{25}H_{28}Sn$, 1), 351 ($C_{18}H_{15}Sn$, 100), 197 (C_6H_5Sn, 33), 154 ($C_{12}H_{10}$, 20), 97 (C_7H_{13}, 19) 77 (C_6H_5, 13), 55 (C_4H_7, 22).

Reaction of 4-(Triphenylstannyl)-2,4-dimethyl-2-pentene (10) with *n*-Butyllithium and Phenyllithium. In a glovebox a 5-mm NMR tube fitted with a high vacuum adaptor was charged with 67 mg of triphenyl(1,1,3,3-tetramethylallyl)tin (**10**) and 1 equiv, 17 mg, of *N,N,N′,N′*-tetramethylethylenediamine. This mixture was brought to the bottom of the tube and to a clean surface on an upper part of the tube was placed 1 equiv, 12.5 mg, of phenyllithium ^6Li. The tube was then closed and removed from the box, and following the mixing of reactants was dipped into liquid nitrogen. The tube was then fitted to a vacuum line and evacuated of argon. Diethyl ether–d_{10}, 0.5 mL, was then vacuum transferred into the tube which was then sealed. The reaction mixture was allowed to stand at room temperature for 22 days. The proton magnetic spectrum of the allylic resonances indicated about 25% allyltin starting material ($\delta = 5.48$ ppm, m, $^4J(CH_3{-}CH) = 1.28$ Hz, $^3J(Sn{-}CH) = 30.34$ Hz), about 25% hydrosylate, 2,4-dimethyl-2-pentene ($\delta = 4.944$ ppm, m, ^4J(exo $CH_3{-}CH) = 1.18$ Hz, ^4J(endo $CH_3{-}CH) = 1.33$ Hz, $^3J((CH_3)_2{-}CH) = 6.66$ Hz), and about 50% of an unidentified allylic resonance ($\delta = 5.22$ ppm, m, $J = 1.35$ Hz). An additional two unknown multiplet resonances at 1.75 and 1.693 ppm were observed.

In a glovebox a 5-mm NMR tube fitted with a high vacuum adaptor was charged with 67 mg of triphenyl(1,1,3,3-tetramethylallyl)tin (**10**) and 1 equiv, 17 mg, of *N,N,N′,N′*-tetramethylethylenediamine. This mixture was brought to the bottom of the tube and to it was then added *n*-butyllithium-^6Li (0.034 mL, 4.4 M, pentane) dropwise and from a syringe. The tube was closed and removed from the box, and its contents were mixed together prior to immersion in liquid nitrogen. The tube was fitted to a high vacuum line and evacuated of argon. Diethyl ether-d_{10}, 0.5 mL, was then vacuum transferred into the tube which was then sealed. The proton NMR spectrum of this mixture after standing at room temperature for 20 h indicated the presence of a single allylic resonance coupled to tin ($\delta = 5.27$ ppm, $^3J(H{-}Sn) = 30.3$ Hz) and the presence of resonances in the aromatic region, $\delta = 7.98$ ppm (m, 1 H, $J = 6.35$ Hz) and $\delta = 7.02{-}6.93$ ppm (m, 2 H), characteristic of phenyllithium.

(1,1,3,3-Tetramethylallyl)lithium–TMEDA (11). A 50-mL Schlenk tube containing a glass-coated stir bar was flamed and cooled under vacuum. The flask was transported into a glovebox where it was charged with 0.050 g (0.192 mmol) of **9** and 0.022 g (0.189 mmol) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA). The flask was removed from the box and placed in a dry ice bath at −92 °C. Under a flow of argon the flask was then opened and 1.85 mL of diethyl ether and 0.15 mL of tetrahydrofuran (ca. 10 molar equiv of THF per mol of **9**) were added for solvation. Methyllithium (0.1 mL, 1.6 M, diethyl ether) was then added dropwise and slowly from a syringe to the reaction flask. The reaction was allowed to proceed for 0.5 h at −92 °C. At this point the glass stopper was replaced with a high vacuum stopcock adaptor and the flask was connected to a high vacuum line. Evaporation of THF, diethyl ether, and $(CH_3)_4Sn$ at −92 °C was realized over 8 h. The reddish color of the allylic complex became faintly yellow when the solvents were fully evaporated. The powdery residue was then taken up in 2 mL of vacuum-transferred *n*-pentane. The reaction apparatus was transferred back into a glovebox, where unreacted MeLi was filtered by passing the solution through a Pasteur pipet stoppered with tightly packed glass wool. The yield of **11** is estimated at 85%. Aliquots of **11** in NMR tubes can then be used for spectroscopic studies following evaporation of *n*-pentane and vacuum transfer of deuterated solvent. ^{13}C NMR (ppm, diethyl ether-d_{10}, 296 K): C1 and C3 59.72, C2 138.28, allylic CH_3s 25.85, NCH_3 46.27, NCH_2 58.12. ^1H NMR: CH_3s 1.76 (s), allylic CH 5.386 (s), NCH_3 2.219 (s), NCH_2 2.373 (s).

2,2,4-Trimethyl-1-phenylpent-3-en-1-ol (13). A solution containing diethyl ether, 1.8 mL, THF, 0.2 mL, TMEDA, 0.036 g, and 4-(trimethylstannyl)-2,4-dimethyl-2-pentene (0.8 g, 0.31 mmol) was reacted with an equivalent amount of methyllithium (0.22 mL, 1.4 M, diethyl ether) at −78 °C over 2 h. Benzaldehyde (0.032 g, 0.302 mmol) was then added and the reaction was allowed to proceed for $^1/_2$ h before warming to room temperature. The reaction was then quenched with excess 0.1 N HCl and the organic phase was extracted with diethyl ether. Concentrating under vacuum yielded a viscous liquid containing **13** in 81% yield (0.049 g) together with 19% of α-phenylethanol based on methyllithium. ^1H NMR ($CDCl_3$, ppm): $C{=}C\mathit{H}{-}$ 5.149 (m, 1 H, $^4J((CH_3)_2C{=}CH) = 1.65$ Hz), endo CH_3 1.738 (d, 3 H), exo CH_3 1.727 (d, 3 H), $-C(C\mathit{H}_3)_2-$ 1.05 and 1.039, $C{-}O\mathit{H}$ 2.07 (bs), $-C(OH)\mathit{H}-$ 4.573 (b, 1 H, $^3J(OH{-}CH) < 1$ Hz), Ar 7.24–7.36.

9,10-Dihydro-9-(1,1,3-trimethyl-2-butenyl)anthracene (14). A dry 50-mL Schlenk tube with a glass-coated stir bar was charged with 1.8 mL of diethyl ether and 0.2 mL of tetrahydrofuran. Samplings of 0.20 mmol each of *N,N,N′,N′*-tetramethylethylenediamine (23 mg) and trimethyl(1,1,3,3-tetramethylallyl)tin (52 mg) were added to the solution, and the flask was then brought to −78 °C with an external bath. Methyllithium (0.14 mL, 1.4 M, diethyl ether) was then added dropwise from a syringe to generate **11**. After 3.6 h, 1 equiv of anthracene, 35.5 mg, was then added neat to the anion. Within minutes the bright orange color of the anion began to change to red, indicating the presence of alkenylated anthracene anion. The reaction was allowed to proceed for 4 h, when it was then quenched with excess water and washed free of the diamine. The oily organic phase was analyzed by NMR for the presence of allylic resonances whose integration indicated a yield of 82% of **14**. The oily residue was then purified (38.5 mg) by column chromatography. ^{13}C NMR ($CDCl_3$, ppm): C1 127.63, C2 and C3 124.88 and 125.86, C4 130.69, C9 36.45, C10 28.81, $-\mathit{C}(CH_3)_2-$ 32.27, $-C(\mathit{C}H_3)_2-$ 28.08, $-\mathit{C}H{=}C(CH_3)_2$ 131.29, $-CH{=}\mathit{C}(CH_3)_2$ 132.33, $-CH{=}C(\mathit{C}H_3)_2$ 21.77 and 18.43. ^1H NMR: $H10_{ax}$ 4.43 (d, 1 H), $H10_{eq}$ 3.96 (d, 1 H), $H9_{eq}$ 4.11 (s, 1 H), $-C(C\mathit{H}_3)_2-$ 1.33 (s, 6 H), $-C\mathit{H}{=}C(CH_3)_2$ 5.156 (m, 1 H), endo CH_3 1.896, exo CH_3 1.693, H1–H4 7.52–7.40 ($^4J(CH{=}C{-}{=}C(CH_3)_2) = 1.22$ Hz; $^2J(H10_{ax}{-}H10_{eq}) = -18.70$ Hz). MS: M^+ 276 (0), 179 (100, $C_{14}H_{11}$), 97 (48, C_7H_{13}).

Attempted Generation of 9,10-Dihydro-9-butylanthracene. A dry 50-mL Schlenk tube with a glass-coated stir bar was charged with 3.6 mL of diethyl ether and 0.4 mL of tetrahydrofuran. Under a flow of argon were then added samples of 0.061 g of *N′,N′,N,N*-tetramethylethylenediamine, 0.525 mmol, and 0.094 g of anthracene, 0.525 mmol. The reaction flask was stoppered and the mixture cooled to −78 °C with an external bath. An equivalent of *tert*-butyllithium (0.33 mL, 1.6 M, pentane) was then added dropwise from a syringe again under a flow of argon. The reaction flask was stoppered and the reaction allowed to proceed for 2 h. The reaction was then quenched with excess H_2O and allowed to warm to room temperature. The organic phase was then extracted, dried over $MgSO_4$, and concentrated under vacuo. Proton NMR analysis of the products revealed solely anthracene and the diamine.

The same procedure was repeated using 4 mL of tetrahydrofuran as the reaction solvent and was quenched with ^2H_2O. No evidence of any dihydroanthracene or of deuterated anthracene was detected by proton NMR analysis.

The above initial procedure was again repeated and *n*-butyllithium (0.33 mL, 1.6 M, pentane) was used as the alkylating agent. Again, no evidence of a dihydroanthracene was detected.

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Supplementary Material Available: ^1H NMR spectra for compounds **7**, **9**, **10**, **11**, and **14**, ^{13}C NMR spectra for compounds **7**, **9**, **10**, and **11**, and mass spectra for compounds **7**, **9**, **10**, and **14** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

4,6-Dinitro-7-methylbenzofuroxan: A Strong Carbon Acid of Very Low Intrinsic Reactivity

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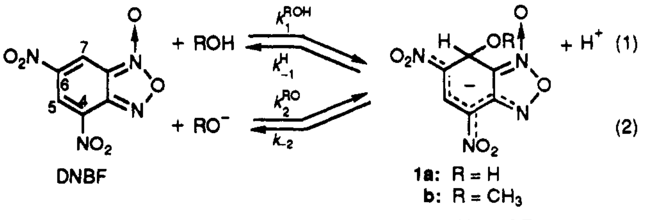
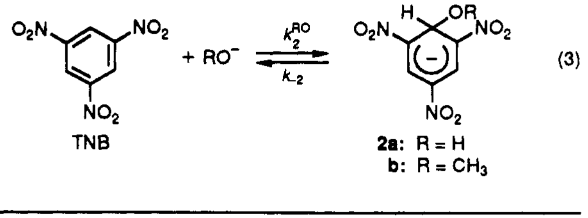
Rates of ionization of 4,6-dinitro-7-methylbenzofuroxan (**3**) by water, hydroxide ion, and various general bases have been measured in aqueous solution at $t = 25$ °C. The solvent pathway is the major process contributing to the formation of the resulting carbanion (C-3) in solutions of pH ≤ 8. The very high thermodynamic stability of C-3 (p$K_a^{CH} = 2.50$), the exocyclic carbon of which is essentially olefinic in nature, is shown to derive for the most part from an extensive delocalization of the negative charge through the two nitro groups and the annelated furoxan ring. In agreement with the idea that considerable molecular, electronic, and solvational reorganization is required to produce a highly delocalized carbanion, the deprotonation of **3** is associated with one of the highest intrinsic energy barriers for proton transfer so far measured in aqueous solution ($\Delta G_0^{\ddagger} = 85.5$ kJ mol^{-1}). The strong acidity of **3** also emphasizes the exceptional activating effect of a 4,6-dinitrobenzofuroxan moiety.

There is much evidence that dinitrobenzofuroxan derivatives are extremely electron-deficient and therefore very "acidic" heteroaromatics.[1-10] The high tendency of 4,6-dinitrobenzofuroxan (DNBF) to undergo σ-complexation in the absence of any added base in aqueous or methanolic solution is illustrative for this behavior.[3,4] The pK_a's for the formation of the hydroxy and methoxy adducts **1a** and **1b** according to eq 1 are equal to 3.75 (t = 25 °C) and 6.45 (t = 20 °C), respectively, in the corresponding solvents. This makes these σ-complexes about 10^{10} times more stable than the analogous adducts **2a** and **2b** of 1,3,5-trinitrobenzene, which are the common references in σ-complex chemistry.[3,4] Use of alkali hydroxide or methoxide solutions is in fact necessary to achieve the formation of **2a** and **2b** in water and methanol, respectively (eq 3).[11]





Two main factors are believed to contribute to the exceptional ease of formation and stability of **1a** and **1b**.[1,2] The first is the relatively low aromaticity of the benzofuroxan system which is expected to favor the covalent addition compared to most aromatic and heteroaromatic systems. The second factor is the combination of the strong electron-withdrawing effects of the two nitro groups and the annelated furoxan ring. The result is not only a high electron-deficiency at C-7 of DNBF, and hence a high susceptibility of this ring position to nucleophilic attack, but also a high electron-delocalizing capability of the negative charge which enhances the stability of the resulting σ-adducts.

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