Separation of Closely Boiling Isomers and Identically Boiling Isotopomers via Electron-Transfer-Assisted Extraction

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Mixtures of isotopomers with identical molecular weights (ethyl- d_5 -benzene + ethylbenzene- d_5 and tert-butyl- d_9 biphenyl + *tert*-butylbiphenyl- d_9) have been partially resolved by making use of their differing solution electron affinities. EPR analysis of the anion radicals resulting from the partial potassium reduction of mixtures of the isotopomers (*R and R, respectively) in tetrahydrofuran show that the equilibrium constant for the reaction R^{•-},M⁺ $+ *\mathbf{R} = \mathbf{R} + *\mathbf{R}^{-}, \mathbf{M}^{+}$ deviates from unity. These EPR results predict that a separation of anion radical from neutral molecule would effect a separation of the isotopomers. Removal of the solvent leaves a solid mixture of neutral and potassium anion radical salt forms of the isotopomers. Subsequent dissolution of the neutral materials from the anion radical salts yields a mixture that is enriched in the ring-deuterated isotopomer, and reoxidation of the anion radical with iodine yields a mixture that is enriched in the ring-protiated isotopomer. Analogous experiments were also used to separate closely boiling geometric isomers.

Due, in part, to industrial needs, the development of nondestructive separation techniques for closely boiling isomeric mixtures remains an ongoing challenge in separation science. Examples of such mixtures include aromatics (i.e., *o*-xylene, *p*-xylene, ethylbenzene), dichlorinated toluenes, and alkylsubstituted biphenyls.¹ Other examples are isotopic in nature, such as H_2O/D_2O and $H_2^{16}O/H_2^{18}O.^2$

One of the most attractive separation processes is extractive distillation.^{3a} Extractive distillation utilizes the addition of a third component to a mixture of two closely boiling components. This process is most effective for two closely boiling components that are different in chemical nature. However, this separation process cannot be successfully applied to isomers because the entrainer has about the same effect on each of the components and therefore does not change their relative volatility.

Alternative techniques must therefore be investigated for the separation of mixtures of isomers. Some alternatives include the following: (i) mixed extractive entrainers^{3b,4} (this is an effective

method for separating ethylbenzene from *m*- and *p*-xylene); (ii) fractional crystallization^{5–12} (this method employs differences in freezing points); (iii) fractional crystallization used in conjunction with catalytic isomerization;^{13–16} (iv) membrane permeation;^{17,18} (v) adsorption^{19,20} (the Universal Oil Products (UOP) "Parex" process for separating *m*- and *p*-xylenes), and the recently reported electrochemically modulated chromatography,²¹ the UOP "Ebex" process for separating ethylbenzene from *m*- and *p*-xylenes;²² (vi) reactive distillation which makes use of chemical differences (i.e., selectivity) between the isomers and a third component, the reactive entrainer.^{3a}

An example of the reactive distillation process is the separation of *m*- and *p*-xylene isomers.^{3a} Organosodium-exchange reactions of this type (reaction 1) are reversible and fast and involve

$$R_1H + R_2^{-}, Na^+ \rightleftharpoons R_2H + R_1^{-}, Na^+$$
 (1)

organometallic compounds with very low vapor pressures. In reaction 1, the sodium preferentially binds to the stronger acid component. The key to attaining a rapid equilibrium is the introduction of a chelating agent which will complex with the organosodium compounds. The crown ether, 18-crown-6, was chosen for this particular purpose. Also, a hydrocarbon solvent,

- (5) Meek, P. D. In Advances in Petroleum Chemistry and Refining; McKetta, J. J., Ed.; Interscience: New York, 1961; Vol. 4.
- (6) Wolfe, P. Commun. ACM 1959, 2, 12.
- (7) Chem. Eng. News 1968, 46, (40, Sept 16), 50.
- (8) Machall, E. F. U.S. Patent 3 798 282, 1972.
- (9) Oden, E. C. U.S. Patent 3 788 819, 1974.
- (10) Benris, A. G. U.S. Patent 3 798 283, 1972.
- (11) Egan, C. J.; Luthy, R. V. Ind. Eng. Chem. 1955, 47, 250.
- (12) Schaeffer, W. D.; Dorsey, W. S. In Advances in Petroleum Chemistry and Refining, McKetta, J. J., Ed.; Interscience: New York, 1962; Vol. 6.
- (13) Hahn, A. The Petrochemical Industry, McGraw-Hill: New York, 1970.
- (14) Brownstein, A. U. S. Petrochemicals, Petroleum Publishing Co.: Tulsa, OK, 1972.
- (15) Goldstein, R. F.; Waddams, A. L. *The Petroleum Chemicals Industry*, 3rd ed.; F. N. Spon Ltd.: London, 1967.
- (16) Waddams, A. L. Chemicals from Petroleum; The Noyes Press: Pearl River, NY, 1962.
- (17) Choo, C. Y. In Advances in Petroleum Chemistry and Refining, McKetta, J. J., Ed.; Interscience: New York, 1967; Vol. 6.
- (18) Kikic, I.; Alessi, P.; Visalberghi, M. O. Inst. Chem. Eng. Symp. Ser. 1978, No. 54, 139.
- (19) Winnick, J. Chem. Eng. Processes 1990, 41.
- (20) Rosset, A. J. U.S. Patent 3 665 046, 1972.
- (21) Deinhammerf, R. S.; Ting E. Porter, M. D. Anal. Chem. 1995, 67, 237.
- (22) de Rosset, A. J.; Neuzil, R. W.; Tajbl, D. G.; Braband, J. M. Sep. Sci. Technol. 1980, 15, 637.

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⁽¹⁾ Tyreus, B. D.; Luben, W. L. Chem. Eng. Commun. 1982, 16, 91.

⁽²⁾ Huffman, J. R.; Urey, H. C. Ind. Eng. Chem. 1937, 29, 531.

 ^{(3) (}a) Doherty, M. F.; Sylvester, L. F.; Terrill, D. L. Ind. Eng. Chem. Processes Des. Dev. 1985, 24, 1062. (b) Berg. L.; Kober, P. J. AICheE J. 1980, 26, 862.

⁽⁴⁾ Berg, L. AIChE J. 1983, 29, 694.

³⁸⁸⁰ Analytical Chemistry, Vol. 70, No. 18, September 15, 1998

such as cumene, needs to be introduced in order to dissolve the crown ether complex. Gau and Marquez have studied these transmetalation reactions when R_1 is *m*-xylene and R_2 is *p*-xylene. The transmetalation reaction reported is shown in reaction 2.²³



Reaction 2 illustrates the fact that *m*-xylene $[m-C_6H_4(CH_3)_2]$ is more acidic than *p*-xylene; therefore, the sodium preferentially binds to the *m*-xylene, leaving the *p*-xylene $[p-C_6H_4(CH_3)_2]$ free to boil overhead in a distillation column. These results as well as those of Deinhammerf et al.²¹ motivated us to investigate the feasibility, in terms of thermodynamics, of effecting analogous chemical separations via a simple electron transfer. Such a process would not involve any chemical change of the substrates other than the addition of an electron and would rely upon the nonunity value of the K_{eq} for an electron transfer (reaction 3) as opposed to a proton transfer as in reaction 1. Hence, the separation technique investigated here would rely upon the differences in solution electron affinity as opposed to differences in acidity.

$$\mathbf{R}_1 + \mathbf{R}_2^{\bullet-}, \mathbf{Na}^+ \rightleftharpoons \mathbf{R}_2 + \mathbf{R}_1^{\bullet-}, \mathbf{Na}^+$$
(3)

Over two and a half decades ago Szwarc and co-workers²⁴ used EPR as an analytical tool for the evaluation of the relative concentrations of the anion radicals of β -ethylnaphthalene and α -ethylnaphthalene, in the presence of the neutral molecules. In tetrahydrofuran (THF), the free energy change for reaction 4



proved to be -600 cal/mol with a reported experimental error of only ~ 10 cal/mol.²⁴ The nonunity value of K_{eq} for reaction 4 means that any separation of the anionic material from equilibrated neutral material would also represent a partial separation of the two isomers.

A separation scheme based upon solution electron affinity has another potential application: it could lead to better techniques for the separation of isotopomers. Hydrocarbon isotopomers, which have identical masses, are impossible to separate via the usual physical means since their vapor pressures and diffusion and effusion properties are nearly identical. Hence chemical means must be utilized. The thermochemical properties of isotopomers can be very different. For example, the enthalpy difference between $(CD_3)_2C^+$ -CH $(CH_3)_2$ and $(CH_3)_2C^+$ -CH $(CD_3)_2$ is 419 cal/mol.²⁵ We have coupled analogous thermochemical



Figure 1. Actual (lower) EPR spectrum recorded at 190 K of a 1:1.78 ratio of a ethyl-*d*₅-benzene/ethylbenzene-*d*₅ mixture in DME reduced by a very deficient amount of potassium metal. The simulated (upper) EPR spectrum was generated using a 1.0:0.6 ratio of anion radicals (ethyl-*d*₅-benzene⁺⁻/ethylbenzene-*d*₅^{*-}) suggesting an equilibrium constant for reaction 5 of 0.34. Coupling constants (in G): used for ethyl-*d*₅-benzene^{*-} simulation, *a*_(H) = 4.95 (2H), *a*_(H) = 4.63 (2H), *a*_(H) = 0.70 (1H), *a*_(D) = 0.11 (2D); used for the ethylbenzene-*d*₅^{*-} simulation, *a*_(D) = 0.82 (2D), *a*_(D) = 0.78 (2D), *a*_(D) = 0.114 (1D), *a*_(H) = 0.70 (2H).

differences with the fact that deuteriation at nonequivalent sites can drastically alter the chemistry of radical anions²⁶ to separate hydrocarbon isotopomers that would be nearly impossible to separate by physical means.

Since the thermochemistry of electron attachment to benzene²⁷ and to the polyarenes²⁸ has been shown to be made less favorable upon isotopic perturbation, we were motivated to utilize this thermochemical difference to probe the relative solution electron affinities of alkyl-substituted benzene and biphenyl isotopomers. We further hoped to take advantage of any electron affinity differences to develop a means for partial separation of these isomers.

RESULTS AND DISCUSSION

When 5 mL of dimethoxyethane (DME) solution that is 0.100 M in ethyl-*d*₅-benzene (C₂D₅-C₆H₅) and 0.178 M in ethylbenzene*d*₅ (C₂H₅-C₆D₅) containing a very molar deficient amount of 18crown-6 (18-C-6) is exposed to a freshly distilled potassium metal mirror under high vacuum, a stable solution of both anion radicals (C₂D₅-C₆H₅^{•-} and C₂H₅-C₆D₅^{•-}) and neutral materials is formed. The concentration of anion radical cannot exceed the concentration of 18-C-6 as potassium metal will not reduce ethylbenzene at ambient temperature in the absence of crown ether. The ESR spectrum of the anion radical of ethylbenzene has been previously recorded,²⁹ and our mixture of anion radicals (Figure 1) is best simulated using a ratio of concentrations ([C₂D₅-C₆H₅•^{•-}]/[C₂H₅-

⁽²³⁾ Gau, C.; Marquez, S. J. Am. Chem. Soc. 1976, 98, 1538.

⁽²⁴⁾ Moshuk, G.; Connor, H. D.; Szwarc, M. J. Phys. Chem. 1972, 76, 1734.

⁽²⁵⁾ Saunders, M.; Cline, G. W. J. Am. Chem. Soc. 1990, 112, 3955.

⁽²⁶⁾ Guthrie, R. D.; Shi, B. J. Am. Chem. Soc. 1990, 112, 3136.

^{(27) (}a) Stevenson, C. D.; Espe, M. P.; Reiter, R. C. J. Am. Chem. Soc. 1986, 108, 532. (b) Stevenson, C. D.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. J. Am. Chem. Soc. 1989, 111, 6578.

^{(28) (}a) Stevenson, C. D.; Espe, M. P.; Reiter, R. C. J. Am. Chem. Soc. 1986, 108, 5760. (b) Godnow, T. T.; Kaifer, A. E. J. Phys. Chem. 1990, 94, 7682. (c) Stevenson, C. D.; Sturgeon, B. E.; Vines, K. S. J. Phys. Chem. 1988, 92, 6850. (d) Stevenson, C. D.; Sturgeon, B. E. J. Org. Chem. 1990, 55, 4090. (e) Stevenson, C. D.; Rice, C. V. J. Am. Chem. Soc. 1995, 117, 10551.

⁽²⁹⁾ Bolton, J. R.; Carrington, A.; Forman, A.; Orgel, L. E. Mol. Phys. 1962, 5, 43.



Figure 2. Percentage of $C_6D_5C_2H_5$ in mixtures containing $C_6D_5C_2H_5$ and $C_6H_5C_2D_5$ vs the percentage that the m/z = 96 peak makes up of the sum of the intensities of the m/z = 96 and m/z = 93 peaks. The solid circles represent the mass spectral results for phase I and phase II resulting from the isotopomer separation process. Note that the percentage of $C_6D_5C_2H_5$ is higher in the neutral phase (phase I) than it is in the anionic phase (phase II).

 $C_6D_5^{\bullet-}$]) that is 1.0/0.60 at 190 K. This ratio implies that the equilibrium constant for reaction 5 is 0.34. Five such experiments

$$H \bigoplus_{H} \bigoplus_{H} CD_{2}CD_{3} D \bigoplus_{D} CH_{2}CH_{3}$$

$$H \bigoplus_{H} \bigoplus_{H} CD_{2}CD_{3} D \bigoplus_{D} CH_{2}CH_{3}$$

$$H \bigoplus_{H} \bigoplus_{H} CD_{2}CD_{3} D \bigoplus_{D} CH_{2}CH_{3}$$

$$(5)$$

show that $K_{\rm eq} = 0.30 \pm 0.03$ for reaction 5 at 190 K, where the error represents the standard deviation in the measured values for $K_{\rm eq}$.

Attempts to separate the anionic material (phase II) from the neutral material (phase I) after removal of the solvent were severely hampered due to the instability of the K+(18-C-6)ethylbenzene⁻⁻ salts toward return of the electron to the metal leaving a simple mixture of 18-C-6, ethylbenzene, and potassium metal. In a particular experiment, a mixture of 2.34 mmol of both C_2D_5 - C_6H_5 and C_2H_5 - C_6D_5 were reduced with ultrapure potassium metal in 20 mL of THF containing 1.73 mmol of 18-C-6. The solvent was removed under high-vacuum conditions while the solution was maintained at -43 °C. This is the lowest temperature at which THF has a sufficient vapor pressure for removal. Hexane at -43 °C was used to extract the neutral ethylbenzenes, which were labeled phase I, from the solid anion radical salts. Iodine in diethyl ether was added to the solid anion radical salts to cause reoxidation to the ethylbenzenes $[^{1}/_{2}I_{2}$ + $R^{\bullet-},(18\text{-C-6})K^{+}_{(solid)} \rightarrow$ $(18-C-6_{(solid)} + KI_{(solid)} + R_{(liq)}]$, which were labeled phase II. Mass spectral analysis (Figure 2) of the two phases showed that phase II was enriched and phase I accordingly depleted in the ethyl- d_5 benzene. Thus, $\alpha = 0.84 = \{ [C_6H_5C_2D_5] / [C_6D_5C_2H_5]_{(\text{phase I})} \} /$



Figure 3. GC traces and the *tert*-butyl region of the ¹H NMR spectra (above) of the original mixture (standard), phase II (anionic phase), and phase I (neutral phase) resulting from a separation process carried out on a mixture of *m*- and *p*-*tert*-butylbiphenyl based on Reaction 6. The first GC peak is due to *m*-*tert*-butylbiphenyl, and the second is due to *p*-*tert*-butylbiphenyl. Likewise, the low-field NMR peak is due to the *m*-*tert*-butyl group, and the higher field peak is due to the *p*-*tert*-butyl group.

{[C₆H₅C₂D₅]/[C₆D₅C₂H₅]_(phase II)} for this particular experiment. If the efficiency of the separation was 100% and the thermodynamic equilibrium remained the same in the solid phase, the separation factor (α) would be the same as K_{eq} for reaction 5 at -43 °C. However, it has been well established that α values obtained from solid-state separations are larger than the thermodynamic equilibrium constants found in solution for these anion radical systems.^{28d} Nevertheless, this is an encouraging separation factor for a system consisting of isotopomers (with identical masses).³⁰

As indicated in the introduction, we were interested in extending the possible utility of this technique to geometrical isomers. The Friedel–Crafts addition of *tert*-butyl chloride to biphenyl leads to a mixture of *m*- and *p*-*tert*-butylbiphenyls, which are very difficult to separate but easy to analyze via ¹H NMR. In our hands, the Friedel–Crafts additions resulted in the expected mixture of *m*- and *p*-*tert*-biphenyls, which GC and proton NMR analysis (Figure 3) show to be 31% *p*-*tert*-biphenyls. This mixture was then reduced with an ~50% molar deficient amount of potassium metal in THF, which resulted in the equilibrated electron-transfer reaction (reaction 6). After removal of the solvent



under reduced pressure, freshly distilled hexanes were added in order to remove the neutral materials (labeled phase I) from the anionic material. The anionic materials were subsequently reoxidized to the neutral state by the addition of I_2 dissolved in diethyl ether and labeled phase II.

From GC and NMR analysis, it is evident that the neutral phase (phase I) is depleted in *p-tert*-butylbiphenyl and enriched in the

⁽³⁰⁾ The molecular masses of the isotopomers actually differ very slightly due to relativistic effects, but this was not considered.

m-*tert*-butylbiphenyl (Figure 3). Conversely, phase II is depleted in the *m*-*tert*-butylbiphenyl and enriched in the *p*-*tert*-butylbiphenyl. The proton NMR spectra confirm the GC results (Figure 3), and both analytical techniques show $\alpha = \{[meta]/[para]_{(phase II)}\}/$ $\{[meta]/[para]_{(phase I)}\} = 0.36 \pm 0.08$. Hence, solution electron affinity differences can provide an efficient mechanism for isomer separation.

The fact that K_{eq} for reaction 6 is less than unity is explained by the steric interaction between the *m*-*tert*-butyl group and the protons on the unsubstituted phenyl moiety. A PM3 calculation predicts that this interaction increases the dihedral angle between the two phenyl rings to 1.2° in the meta anion radical from 0.079° in the para anion radical. The consequent PM3 predicted K_{eq} for reaction 6 (assuming $\Delta H^{\circ} = \Delta G^{\circ} = -RT \ln K_{eq}$) is 0.47 at 298 K. Due to its size, the *tert*-butyl substituent worked out suitably for this geometric isomer separation study; it is also an ideal candidate for further investigation of the isotopomer problem, as both the ring system and substituent have nine sites for H and D substitution.

Friedel–Crafts additions were carried out separately with *tert*butyl- d_9 chloride and biphenyl and with *tert*-butyl chloride and biphenyl- d_{10} to yield two mixtures: (1) *p-tert*-butyl- d_9 -biphenyl [p-(CD₃)₃C-C₁₂H₉] + *m-tert*-butyl- d_9 -biphenyl [m-(CD₃)₃C-C₁₂H₉] and (2) *p-tert*-butylbiphenyl- d_9 [p-(CH₃)₃C-C₁₂D₉] + *m-tert*-butylbiphenyl- d_9 [m-(CH₃)₃C-C₁₂D₉].

When a mixture (Figure 4) of *p*-tert-butylbiphenyl- d_9 and *p*-tertbutyl- d_9 -biphenyl is reduced with 0.5 equiv of potassium metal in THF at -78 °C, the equilibria shown in reactions 7 and 8 as well as the electron-transfer equilibria between the respective para and meta isomers are established.



After removal of the THF under reduced pressure, freshly distilled hexanes were added in order to remove any neutral isotopomers (phase I) from the anion radicals (phase II). The anion radical material (phase II) was reoxidized by introduction of a molar excess of I_2 dissolved in diethyl ether. Both phases were submitted to 300-MHz proton NMR analysis.

The integration of the aromatic region shows the relative amount of *tert*-butylbiphenyl- d_9 present. On the other hand, integration of the peaks between 1.3 and 1.7 ppm indicates the relative amount of *tert*-butyl- d_9 -biphenyl present. In comparison to the original mixture of isotopomers (Figure 4), it is evident that the neutral phase is depleted in *tert*-butylbiphenyl- d_9 , while the NMR spectrum of the reoxidized anion radical phase indicates an enrichment in *tert*-butylbiphenyl- d_9 . Again these results correspond to an electron preference for the isotopomer that is not deuterated in the aromatic moiety. This was the expected result, as it has been observed that the equilibrium constant for reaction 9 is 0.51 ± 0.01 at 298 K,³¹ and deuteriation of the β sp³ hybridized carbons should not affect the π -electron attachment.



The separation factor for both the meta- and para-substituted isotopomers is 0.69 ± 0.05 , which agrees quite well with the above arguments. Most likely, the reason that α is greater than K_{eq} for reaction 9 is because the *tert*-butyl group actually replaces one of the deuteriums in the perdeuterated biphenyl.

SUMMARY

It has been shown that solution electron affinity can discriminate between materials of identical molecular weight for both cases of isotopomers and geometrical isomers. Further, this difference in solution electron affinities can be used to realize the physical separation of these materials. To render the solution electron affinity discrimination of practical value in an industrial sense, it would necessary to engineer a continuous extractive or distillation process, which would make use of the very large differences in the vapor pressures or solubilities of the neutral and anionic phases, as described above for the separations based upon relative acidities.

EXPERIMENTAL SECTION

Physical Separations. The separations based upon solution electron affinity differences were all carried out as described below for a particular example. Carefully weighed portions of the tertbutyl- d_9 -biphenyl (150 mg, 6.85×10^{-4} mol) and *tert*-butylbiphenyl d_9 (150 mg, 6.85 \times 10⁻⁴ mol) were placed in bulb A of the apparatus shown in Figure 5. Tube B was charged with enough argon-packed, oil-free, potassium metal to reduce approximately half of the molecules in bulb A. Tube B was sealed at point 1, and the entire apparatus was evacuated. A fresh potassium mirror was deposited in bulb A by distillation from tube B. The tube B was then removed from the apparatus at point 2. Approximately 30 mL of anhydrous THF, dried over NaK2, was distilled into bulb A through the vacuum line. The stopcock was shut, and the apparatus was removed from the vacuum line. The THF solution was exposed to the potassium mirror (\sim 30 min.) until the mirror was completely dissolved. A dark green solution of the anion radical was formed immediately. The THF was then redistilled out of the apparatus through the use of the vacuum line. Next, 10-15 mL of hexane was distilled into bulb A to dissolve the neutral hydrocarbons. The hexane solution was then poured through the porous frit of the apparatus. This washing procedure was repeated two more times to ensure that all the neutral material

⁽³¹⁾ Stevenson, C. D.; Wehrmann, G. C.; Reiter, R. C. J. Phys. Chem. 1991, 95, 901.



Figure 4. (Upper) ¹H NMR spectrum of the mixture of *m*- and *p*-tert-butylbiphenyls obtained from the Friedel–Crafts addition of tert-butyl chloride to biphenyl- d_9 . (Middle) ¹H NMR spectrum of the mixture of *m*- and *p*-tert-butylbiphenyls obtained from the Friedel–Crafts addition of tert-butyl- d_9 . (Middle) ¹H NMR spectrum of the mixture of *m*- and *p*-tert-butylbiphenyls obtained from the Friedel–Crafts addition of tert-butyl- d_9 . (Middle) ¹H NMR spectrum of the mixture of Friedel–Crafts products used in the separation experiment.

had been separated from the anion radical. Bulbs A and C were separated, and the anion radical phase (in bulb A) was reoxidized to the neutral state by addition of I_2 in diethyl ether. The ether solution was stirred in the presence of sodium thiosulfate and gravity filtered. The filtered solution was concentrated and labeled phase II. Both phases were submitted to GC and proton NMR analysis.

Friedel–Crafts Alkylations. The alkylation of aromatic rings, called *Friedel–Crafts* alkylation, is a reaction of very broad scope.¹⁶

However, the use of the Friedel–Crafts alkylation reaction with isotopic compounds requires special precautions in order to avoid exchange with the isotopic positions. The process is described below for the case of *tert*-butyl- d_9 -biphenyl.

The 250-mL round-bottom flask was charged with 1.100 g of AlCl₃·6H₂O, and a stir bar was added. To the 50-mL round-bottom flask was added 2.00 g (1.29×10^{-2} mol) of biphenyl. The bulb was connected to the solid addition arm, and the entire apparatus was evacuated immediately. A light flame was used to gently



Figure 5. Apparatus used to carry out the separations based upon relative solution electron affinity.

warm the round-bottom bulb with stirring of the aluminum chloride. As the catalyst was heated, the powder would begin to bump into the sides due to the molecules of water breaking from their coordination sites with the AlCl₃. Carefully, heating was continued until the catalyst stopped bumping. After a cooling period, the biphenyl in the 50-mL round-bottom flask was poured over into the 250-mL round-bottom flask. While under vacuum, the flask was cooled with a dry ice/acetone solution (-78 °C) and 50 mL of CS₂ was allowed to distill into the flask. After distillation, the apparatus was isolated from the vacuum line, and the solution was allowed to warm to room temperature. The apparatus was then filled with nitrogen gas by use of the bubbler, and positive pressure was maintained in the apparatus. Approximately 1.12 g (1.212 \times 10⁻² mol) of *tert*-butyl- d_9 chloride was added dropwise via syringe into the flask, through the rubber septum, over a 1 h period. After addition of the *tert*-butyl- d_9 chloride, the solution was maintained at ambient temperature with stirring for 10 h. The apparatus was reattached to the vacuum line, and the CS₂ was completely redistilled out of the apparatus.

The residual materials were diluted with cyclohexane and filtered under gravity. The hexanes were evaporated under reduced pressures, and the residual material was subjected to vacuum distillation. Approximately 900 mg of a colorless liquid was collected between the temperatures of 105-112 °C at ~0.01 Torr (17% yield). Mass spectral analysis revealed the liquid to be *tert*butyl-*d*₉-biphenyl. NMR analysis also revealed the compound to be fully deuterated in the *tert*-butyl region (Figure 4). The analogous procedure can also be used to produce the *tert*butylbiphenyl-*d*₉ (Figure 4).

Materials. The ethylbenzene- d_5 and 18-crown-6 were purchased from Aldrich Chemical Co., and the ethyl- d_5 -benzene was purchased from Cambridge Isotope Laboratories. The perdeuterated biphenyl, biphenyl, perdeuterated 2-chloro-2-methylpropane, and 2-chloro-2-methylpropane were purchased from Aldrich Chemical Co. All of these materials were used without further purification. Ultrapure, oil-free, potassium metal was purchased from Aldrich Chemical Co.

Instrumentation. EPR spectra were recorded on a Bruker ER-200 EPR spectrometer equipped with a Bruker ER-4111 variable-temperature controller. Mass spectral data were obtained on a Hewlett-Packard 5790/5970 gas chromatograph/mass spectrometer system containing a 30-m, 0.25-mm-i.d. capillary column of methylphenyl silicone. NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer.

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