

$J = 2$ Hz, 2 H), 3.98 (s, 3 H), 3.13 (s, 6 H); exact mass calcd for $C_{10}H_{13}O_4^{79}Br$ m/e 275.9998, found m/e 276.0003.

Elution was continued as follows: 240 mL of 10% E/H, nil; 160 mL of 10% E/H, 0.46 g (13%) of **6c** as a colorless oil. **6c**: IR (neat) 3534 (m), 2976 (s), 1603 (m), 1449 (s), 1374 (s), 1299 (m), 1287 (m), 1261 (m), 1199 (m), 1127-996 (s, br), 969 (s), 925 (s), 762 cm^{-1} (w); NMR δ 6.51 (d, $J = 2$ Hz, 1 H), 6.13 (AB, $\Delta\nu = 17$ Hz, $J = 11$ Hz, with the downfield component further split into a doublet, $J = 2$ Hz, 2 H), 3.57 (br s, 4 H), 3.27 (s, 3 H), 3.18 (s, 6 H), 2.48 (br s, 1 H).¹⁵

Electrolysis of 4d. A solution of 1 g (0.010 mol) of **4d** in 80 mL of solvent was electrolyzed under the standard conditions¹³ [2061 C, 95% current efficiency]. The methanol was removed in vacuo, 25 mL of water was added, and the residue was extracted with methylene chloride (3×20 mL). Workup afforded a colorless oil which was chromatographed on neutral alumina (activity III, 1.8×20 cm column, slurry packed with 10% ether/hexane) as follows: 260 mL of 10% E/H, nil; 120 mL of 10% E/H, 120 mL of 14% E/H, 1.98 g (86%) of **5d** as white crystals. **5d**: mp 49.5-51 °C; IR (KBr) 2941 (m), 1597 (m), 1443 (s), 1376 (s), 1342 (s), 1227 (s), 1198 (s), 1170 (s), 1130-1028 (br, s), 1002 (s), 971 (m), 943 (s), 872 (m), 810 (m), 709 cm^{-1} (m); NMR δ 5.81 (AB, $\Delta\nu = 19$ Hz, $J = 11$ Hz, with downfield component further split into a doublet, $J = 2$ Hz, 2 H), 4.83 (d, $J = 2$ Hz, 1 H), 3.94 (s, 4 H), 3.61 (s, 3 H), 3.16 (s, 6 H); exact mass calcd for $C_{11}H_{16}O_5$ m/e 228.0997, found m/e 228.0992.

Hydrolysis of 5a. To a solution of 1.0 g (5.1 mmol) of **5a** in 25 mL of tetrahydrofuran was added 12.5 mol of 2% acetic acid. The hydrolysis was followed by VPC and quenched with 10 mL of saturated bicarbonate solution after 1.5 h. Workup afforded 0.73 g (94%) of **7a** as an off-white crystalline solid which was recrystallized from methylene chloride/hexane; mp 50-51 °C (lit.¹⁶ mp 51-52 °C).

Hydrolysis of 5b. To a solution of 1.78 g (8.4 mmol) of **5b** in 50 mL of tetrahydrofuran was added 25 mL of 2% acetic acid. The hydrolysis was followed by VPC and quenched with 30 mL of saturated bicarbonate solution after 1.5 h. The organic layer was separated and the aqueous portion extracted with 2×30 mL of ether. Workup of the combined organic solutions afforded 1.36 g of **7b** as a light-yellow oil. Short-path distillation (70 °C bath, 0.40 mm) afforded 1.30 g (93%) of **7b** as a colorless oil: IR (neat) 3040 (w), 2950 (w), 1678 (s), 1647 (s), 1443 (w), 1368 (m), 1355 (m), 1285 (m), 1235 (w), 1156 (s), 1111 (s), 1071 (s), 1011 (s), 963 (s), 940 (m), 869 (w), 810 cm^{-1} (m); NMR δ 6.38 (AB, $\Delta\nu = 31$ Hz, $J = 10$ Hz, with the downfield component further split into a doublet, $J = 3$ Hz, 2 H), 6.35 (m, 1 H), 4.05 (s, 4 H), 1.83 (d, $J = 2$ Hz, 3 H); exact mass calcd for $C_9H_{10}O_3$ m/e 166.0630, found m/e 166.0635.

Hydrolysis of 5c. To a solution of 1.69 g (6.1 mmol) of **5c** in 25 mL of tetrahydrofuran was added 12.5 mL of 2% acetic acid. The hydrolysis was followed by VPC and quenched with 20 mL of saturated bicarbonate solution after 40 h. The organic layer was separated, and the aqueous layer was extracted with 20 mL of ether. Workup of the combined organic solutions afforded 1.38 g of an oily solid shown to be a 10:1 mixture of **7c** and **8c** (not rigorously characterized) by NMR. Recrystallization from carbon tetrachloride afforded 1.10 g (78%) of **7c** as white needles: mp 81-82 °C; IR (KBr) 3115 (w), 3030 (w), 2941 (w), 1675 (s), 1639 (m), 1608 (m), 1366 (m), 1325 (s), 1264 (m), 1209 (m), 1135 (s), 1110 (s), 1088 (m), 1003 (s), 965 (s), 947 (s), 819 (s), 796 (m), 775 cm^{-1} (w); NMR δ 7.03 (d, $J = 3$ Hz, 1 H), 6.51 (AB, $\Delta\nu = 25$ Hz, $J = 10$ Hz, with the downfield component further split into a doublet, $J = 3$ Hz, 2 H), 4.12 (s, 4 H); exact mass calcd for $C_8H_7O_3^{79}Br$ m/e 229.9578, found m/e 229.9583.

Monohydrolysis of 5d. To a solution of 1.5 g (6.6 mmol) of **5d** in 25 mL of tetrahydrofuran was added 12.5 mL of 2% aqueous acetic acid. The hydrolysis was followed by VPC and quenched with 20 mL of saturated sodium bicarbonate. Workup gave 1.15 g of an oily solid which was ca. 7:1 mixture of **8d** and an uncharacterized compound (presumably **7d**). Recrystallization of this material from ether/hexane gave 0.83 g (68%) of **8d** as white crystals, mp 62-64 °C (lit.^{3b} mp 63.5-64.5 °C).

Acknowledgment. We thank the National Science Foundation for support of this work.

Registry No. **1a**, 150-76-5; **1b**, 14786-82-4; **1c**, 17332-12-6; **1d**, 2033-89-8; **4a**, 5394-57-0; **4b**, 75714-41-9; **4c**, 75714-42-0; **4d**, 61711-86-2; **5a**, 75714-43-1; **5b**, 75714-44-2; **5c**, 75714-45-3; **5d**, 75714-46-4; **6a**, 75714-47-5; **6b**, 75714-48-6; **6c**, 75714-49-7; **7a**, 35357-34-7; **7b**, 75714-50-0; **7c**, 75714-51-1; **7d**, 75714-52-2; **8c**, 72054-82-1; **8d**, 64701-03-7.

A Boron-Stabilized Carbanion from the Reaction of Trimesitylborane with Strong Bases in Tetrahydrofuran and Dimethyl Sulfoxide

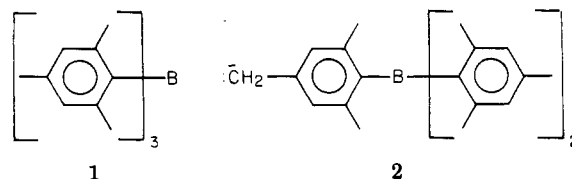
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At the 1980 IUPAC Conference on Boron Chemistry, we presented² the preliminary report of the first spectroscopic observation of a carbanion, obtained from trimesitylborane, **1**, which was clearly stabilized by boron-carbon 2p- π bonding and existed as either an intimate or solvent-separated ion pair. Boron-stabilized "carbanions" have been implicated as intermediates in a number of reactions³, and the syntheses of *B*-(lithiomethyl)-9-borabicyclonane and (3-lithio-2-octenyl)disiamylborane have been reported⁴ as examples of the formation of boron-stabilized "carbanions". More recently, Wilson has reported⁵ the formation of (1-lithioalkyl)dimesitylboranes in tetrahydrofuran (THF) as examples of boron-stabilized carbanions. The degree of ionic character in the carbon-lithium bonds and the extent to which the α boryl substituent stabilized these "carbanions" was not discussed, however, in these papers. We present here a more detailed account of our own results which addresses these questions.

Trimesitylborane, **1**, reacts with *n*-butyllithium or methyllithium in THF and with dimethylsodium or dimethylsodium in dimethyl sulfoxide to form the anion **2**, (4-methylene-2,6,-dimethylphenyl)bis(2,4,6-trimethylphenyl)boron anion.



Solutions of the lithium or sodium salt of **2** in THF or Me_2SO are rose to purple red, depending on concentration, and exhibit a broad absorption band in the visible spectrum, λ_{max} 505 nm ($\log \epsilon$ 4.4). The addition of lithium-

(1) (a) San Francisco State University; (b) The Oregon Graduate Center.

(2) Brian G. Ramsey and Lorne Isabelle, Program Abstracts of International Union of Pure and Applied Chemistry, IMEBORON IV Conf., 1979, p 44.

(3) (a) D. S. Matteson, *Synthesis*, 147 (1975); (b) D. S. Matteson and J. R. Thomas, *J. Organomet. Chem.*, **24**, 263 (1970); (c) G. Cainelli, G. Dal Bello, and G. Zubiana, *Tetrahedron Lett.*, 3429 (1975); (d) G. Zweifel and H. Avzomanian, *ibid.*, 2535 (1966).

(4) M. W. Rathke and R. Kow, *J. Am. Chem. Soc.*, **94**, 6854 (1972); **95**, 2715 (1973).

(5) John Wilson, *J. Organomet. Chem.*, **186**, 297 (1980).

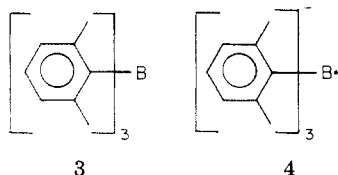
(16) Heller, J. E.; Dreiding, A. S.; O'Connor, B. R.; Simmons, H. E.; Buchanan, G. L.; Raphael, R. A.; Taylor, R. *Helv. Chim. Acta* **1973**, *56*, 272-280.

specific crown ether, 12-crown-4, to solutions of the anion in THF shifts the absorption maximum to 530 nm.

The structure of the anion **2** was established by quenching THF solutions of the anion in D₂O followed by mass spectroscopic and NMR determinations of the percent and position of deuterium incorporation into the recovered trimesitylborane. Although evidence of a reaction between *n*-butyllithium and **1** in THF is immediate in terms of formation of the characteristic color of the anion, the reaction requires several hours for completion. In Me₂SO, formation of the anion is complete in a few minutes.

In a 1-h reaction of 100 mg of **1** in THF with 10 equiv of *n*-butyllithium, after D₂O drowning, 87% of the trimesitylborane was recovered. Seventy percent of this recovered trimesitylborane had incorporated one deuterium as measured by the increase in the (M + 1) 369 mass peak abundance relative to the parent mass peak, 368, in the electron-impact mass spectrum of recovered **1**. Because the parent mass peak of **1** has less than 1% of the abundance of the base peak under electron-impact conditions, the deuterium incorporation was also confirmed by field-ionization/field-desorption mass spectrometry.

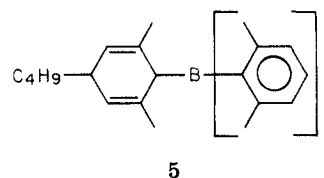
The position of incorporation of deuterium in the trimesitylborane, after quenching of **2** in deuterium oxide, was determined by a combination of ²H and ¹³C NMR to be exclusively in the 4-methyl positions within instrumental limits. The ²H NMR spectrum showed only a *single* resonance with a chemical shift appropriate to the 4-methyl hydrogens of **1**. The assignment of ²H substitution was confirmed by ¹³C NMR spectroscopy with the observation of a ¹³C triplet of equal intensities displaced to the high-field side of the proton-decoupled ¹³C resonance of the 4-methyl carbon. The absence of ²H incorporation into the ortho methyl groups of **1** as well as curiosity concerning the basicity of the "ortho" methyl groups prompted an investigation of the reaction in THF of *n*-butyllithium with tris(2,6-dimethylphenyl)boron, **3**, or tri-*m*-xylylborane. The reaction of **3** with *n*-butyllithium in THF did not, however, produce a boron-stabilized anion, but instead the principal product was the tri-*m*-xylylborane radical anion **4**, readily identified by its ESR spectrum.



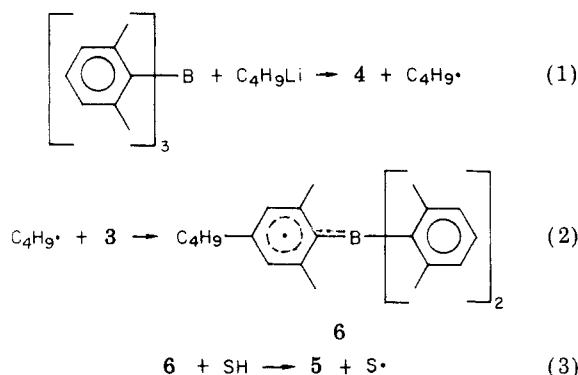
The green colored THF solutions of **4** exhibit a broad absorption band (λ_{\max} 760 nm, $\log \epsilon$ 3.82) in the visible spectrum, similar to that reported for the blue radical anion of **1**, λ_{\max} 800 nm. The 40-nm red shift in the spectrum of **4** on 4-methyl substitution to form the radical anion of **1** suggests that the atomic orbital mixing coefficients at the 4-position carbons are smaller in the transition terminating molecular orbital than in the originating molecular orbital. This is consistent with assignment⁶ of the transition to electron transfer from the half-filled π molecular orbital into the lowest unoccupied π^* molecular orbital which is doubly degenerate and nodal at carbon atoms 1, 1', 1'' and 4, 4', 4'', as well as at boron.

Qualitatively, the reaction of **3** in THF with *n*-butyllithium to form **4** is much slower than the rate of formation of **2** from **1** under the same conditions. Appearance of the

characteristic color of **4** requires 10–15 min and completion of the reaction several days. Quenching of THF solutions of **4** in D₂O or aqueous acetic acid routinely yielded 80% recovery of **4** but without incorporation of ²H detectable by field-ionization mass spectrometry. Combined gas chromatography and mass spectroscopy showed the remaining 20% of material to be a complex mixture of products. The major component of this mixture in all cases was a product of parent mass number 384, corresponding to the addition of the elements of butane to **3**, and whose total mass spectrum is consistent with structure **5**. Since



there is no deuterium incorporation into **5** on quenching, a stable carbanion precursor is unlikely, and we prefer therefore a free-radical mechanism for its formation, eq 1–3.



The results of the reaction of **3** with *n*-butyllithium in THF prompted a reexamination by ESR spectroscopy of the reaction of trimesitylborane with *n*-butyllithium in THF and dimethyl lithium in dimethyl sulfoxide. The THF solutions, which were more than a few hours old, not unexpectedly, exhibit an ESR spectrum characteristic of the well-known trimesitylboron radical anion.⁷ The 1-day-old Me₂SO solutions of **2**, however, exhibit *no* detectable amounts of the radical anion. We estimate the yield of radical anion in THF from the reaction of **1** with *n*-butyllithium as <10%.

The above results strongly imply that the *major* product of the reaction between *tert*-butyllithium and **1** in THF is *not* the radical anion of **1** reported⁸ by Brown and co-workers, since the reported color of the solutions are red, characteristic of the ion **2**, and *not* blue, characteristic of trimesitylboron radical anion in THF. Professor Brown's footnote to our work in the paper⁸ is misleading, therefore, in the potential implication that our work and its conclusions as reported² at the IUPAC conference are incorrect.

Furthermore, the visible spectrum of the "red diamagnetic oligomer" of the trimesitylborane radical anion in benzene, reported by Chu and Weisman,⁹ suggests that this species is also the sodium salt of **2**.

The structural significance of the formation and spectroscopic properties of the anion **2** with respect to boron-carbon 2p- π bonding will be discussed in the remaining

(7) R. G. Griffin and H. Van Willigen, *J. Chem. Phys.*, **57**, 86 (1972), and leading references.

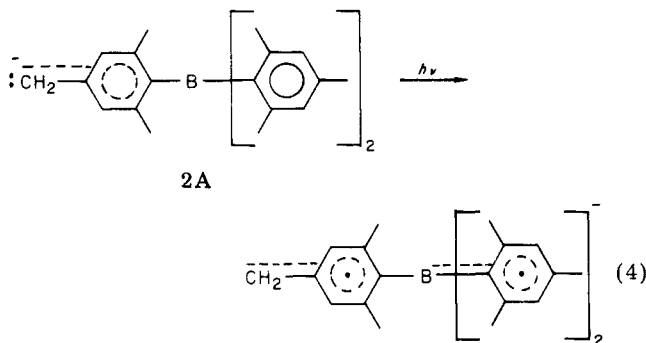
(8) H. C. Brown, G. W. Kramer, J. L. Hubbard, and S. Krishnamurthy, *J. Organomet. Chem.*, **188**, 1, (1980).

(9) T. L. Chu and T. J. Weisman, *J. Am. Chem. Soc.*, **78**, 23 (1956).

(6) Brian G. Ramsey, "Electronic Transitions in Organometalloids", Academic Press, New York, 1969.

paragraphs. The structure and properties of alkali metal derivatives of arylmethyl anions have been extensively investigated by UV-visible¹⁰ and NMR "spectroscopy".¹¹ There seems to be general agreement that benzyllithium exists in THF as a contact ion pair with the lithium ion in close proximity to the methylene carbon, even though extensive delocalization of negative charge into the benzene ring is observed. Other Li⁺ carbanions with greater charge delocalization, such as diphenylmethyl and fluorenyl anions, exist in THF or Me₂SO predominantly as solvent-separated anions, sometimes in equilibrium with detectable amounts of the contact ion pair. The question here is whether the anion **2** more closely resembles a para-substituted benzyllithium species in the THF and Me₂SO with only minor negative charge delocalization into the dimesitylboryl "substituent" or whether the properties of the anion are more consonant with a description of the anion as a delocalized 20 π electron system.

The absorption maximum of **2** is much closer to that of (triphenylmethyl)lithium in THF (λ_{\max} 500 nm)¹² than to that of benzyllithium in THF (λ_{\max} 330 nm).¹² This result is consistent with *excited-state* boron-carbon 2p- π bonding but tells us little about the extent of boron-carbon 2p- π bonding and charge delocalization in the ground state. In direct analogy with the first UV transition of triarylboranes,¹³ the 505-nm transition of **2A** might easily be described in the terms of the charge-transfer model of eq 4.



Perhaps the best chemical evidence of significant carbanion ground-state stabilization in the Li⁺ and Na⁺ salts of **2** is the formation of **2** in Me₂SO, which requires a pK_a of trimesitylborane *less than* 33. Keeping in mind the substantial risks of comparing pK_a's of hydrocarbons determined in different solvents with different bases, the pK_a determined¹⁴ for toluene in cyclohexylamine of 41 suggests a difference in the magnitude of equilibrium C-H acid strength of the order of 10⁷-10⁸ between toluene and trimesityl borane.¹⁵ Physical evidence of substantial accumulation of negative charge at boron comes from a ¹¹B

NMR spectrum of the anion **2** in which the ¹¹B resonance was found to be approximately 48 ppm *upfield* from trimesitylborane.

The electronic transition energy of **2** is significantly independent of both the nature of the cation (Li⁺ or Na⁺) or the solvent (THF or Me₂SO). Such behavior is far more characteristic¹⁶ of solvent-separated ion pairs, such as those of diphenylmethyl or fluorenyl anions, than of contact ion pairs such as those of the benzyllithium in THF, where, for example, PhCH₂Li (λ_{\max} 330 nm) and PhCH₂Na (λ_{\max} 355 nm) maxima are observed.¹⁷ The Li salt of **2** in THF (or Me₂SO) *cannot*, however, exist as a transitional solvent-separated ion pair since the addition of 12-crown-4 ether to THF solutions produces what must of necessity be regarded as the solvent-separated ion pair (λ_{\max} 530 nm). Only very small UV transition-energy differences are expected to exist between "free anions" and solvent-separated anions.

Our best structural rationalization of the available data is that the lithium and sodium salts of the anion **2** are intimate ion pairs in THF or Me₂SO but that substantial charge delocalization on to boron and the steric bulk of the mesityl groups restrict and limit close coordination of the cation to specific sites of high electron density in the anion.

Charge stabilization at a reaction site by a boryl substituent interaction mechanism is highly dependent on the nature of X.¹⁸ Carbanion centers adjacent to B(OR)₂ groups are probably stabilized to a greater extent by the π -electron polarizability of B(OR)₂ than by C-B 2p- π interactions. Where X is aryl, as in the case of **2**, the principal anion-stabilizing interactions possible are the following: (1) π electron charge delocalization into the dimesitylboryl group through B-C 2p- π bonding and (2) a polarizability effect associated with the extensive π -electron system of the arylboryl group. Semiempirical molecular orbital calculations, NMR studies, and PES-determined ionization energies of aryl boranes¹⁸ suggest that B-C 2p- π bonding should make an important contribution to the stability of **2**. The effect of polarizability is more difficult to assess. We believe, nevertheless, that the ion **2** provides a clear-cut example of a boryl substituent groups stabilization of an "ionic" carbanion from a site *nonadjacent* to the incipient carbanion center and the best evidence of ground-state boron-carbon π bonding in an anion.

Experimental Section

Synthesis of Trimesitylborane, 1, and Tri-*m*-xylylborane, 3. These compounds were prepared by reaction of appropriate Grignard reagents with boron trifluoride etherate in ether-benzene mixed solvent. After purification by chromatography on silica gel, melting points of **1** (195-196 °C) and **3** (176-177.5 °C) were obtained in sealed capillaries.

Reactions of 1 with Base. Tetrahydrofuran (THF), after several days reflux, was distilled under nitrogen from lithium aluminum hydride. Spectro-grade dimethyl sulfoxide was first vacuum distilled from calcium hydride, followed by a second distillation from dimethylsodium. Reactions on 50 to 100 mg of borane in 5 mL of solvent were carried out under dry argon using dried glassware fitted with rubber systems through which the

(10) (a) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966); (b) R. Waack, M. A. Doran, and P. E. Stevenson, *ibid.*, **88**, 2109 (1966); (c) W. T. Ford, *ibid.*, **92**, 2857 (1970); (d) S. P. Patterman, I. L. Karle, G. D. Stuckley, *ibid.*, **92**, 1150 (1970).

(11) (a) G. Fraenkel and J. M. Geckle, *J. Am. Chem. Soc.*, **102**, 2869 (1980); (b) D. H. O'Brien, C. R. Russel, and A. J. Hart, *J. Am. Chem. Soc.*, **101**, 633 (1979); **98**, 7427 (1976); (c) R. Waack, L. D. McKeever, and M. A. Doran *Chem. Commun.*, 117 (1969).

(12) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963); *J. Phys. Chem.*, **68**, 1148 (1964).

(13) B. G. Ramsey, *J. Phys. Chem.*, **70**, 611 (1966).

(14) (a) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Am. Chem. Soc.*, **89**, 63 (1967); (b) The pK_a of toluene is provided in A. Streitwieser, Jr., M. R. Granger, F. Mares, and R. A. Wolf, *J. Am. Chem. Soc.*, **95**, 4257 (1973).

(15) It may be noted (ref 15) that in cases where hydrocarbon acids of similar structure and ions of similar aggregate structure are compared, differences between pK_a's as determined relative to fluorene in CHA and Me₂SO are small and 0-1 pK_a units *greater* in cyclohexylamine. This leads to a pK_a estimate for trimesitylborane in cyclohexylamine of 34.

(16) (a) Reference 6, pp 17-20; (b) J. Smid in "Ions and Ion Pairs in Organic Chemistry", 6th ed., Michael Szwarc, John Wiley and Sons, New York, 1972.

(17) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7007 (1975).

(18) (a) B. G. Ramsey and K. Longmuir, *J. Org. Chem.*, **45**, 1322 (1980); (b) B. G. Ramsey and S. J. O'Neill, *J. Organomet. Chem.*, **141**, 257 (1977).

desired base was added by syringe in 5-10 molar excess. Commercial solutions of *n*-butyllithium in hexane and methyllithium in diethyl ether were used. Dimethylsodium was prepared by the reaction of sodium hydride with dry Me₂SO and dimethylsodium by addition of commercial methyllithium in ether to Me₂SO. It was discovered that a dimethylsodium Me₂SO solution exposed to air for only a few minutes remained sufficiently basic to form Ph₃C⁻ from Ph₃CH but would no longer react with 1 to form 2, possibly the result of sodium trimesitylhydroxyborate formation.

Deuterium Oxide Quenching of Anion 2. Deuterium oxide in large excess was added to THF solutions of 2, followed by adjustment of pH to 7 with dilute hydrochloric acid. The solid residue from dried ether extracts of the quenched reaction was chromatographed on silica gel, and the fraction containing 1 was recrystallized from ethanol. GC-mass spectrometry indicated a purity of recovered 1 better than 97%.

Deuterium Oxide Quenching of Radical Anion 4. Quenching of 4 by D₂O followed the procedure outlined for 2. Starting material 3 was recovered in 80% yield based on mass balance. The remaining 20% of material was gas chromatographed on a 3-ft SP 2100 column, temperature programmed between 150 and 300 °C, to yield one major and at least four minor components. The mass spectrum of the major component exhibited a parent ion peak at mass 384 (base peak, mass 221) and other peaks at 327, 325, 278, and 276 mass numbers, consistent with structure 5.

Spectroscopic Measurements. Visible spectra were determined on a Cary 15 UV-visible spectrophotometer.

Electron impact mass spectra was obtained with a Du Pont Model 21-491B GC-MS system operated at 70 eV. Field-ionization mass spectra were obtained with a modified Hitachi RMU-7 mass spectrometer equipped with a field-ionization/field-desorption source at the Oregon Graduate Center, Beaverton, OR.

Nuclear magnetic resonance spectra (²H, ¹³C, and ¹¹B) were carried out on a Varian XL-100 spectrometer at the University of Oregon, Eugene, OR. The ¹¹B spectra were run by utilizing the ¹³C probe and running the spectra without field lock and are, therefore, accurate to only a few parts per million.

Electron spin resonance spectra of the radical anions of trimesitylborane and tris-*m*-xylylborane in THF were obtained on a Varian E-12 spectrometer at San Francisco State University. The ESR spectrum of the radical anion of 1 is well-known⁷ and that of 4 is a similar quarter but with little of the fine structure characteristic of the radical anion of 1. A boron hyperfine splitting constant of 9.2 G was obtained for 4.

Acknowledgment. This work was made possible by a Lubrizol Corporation Grant of the Research Corporation.

Registry No. 1, 7297-95-2; 2, 75700-27-5; 3, 75700-28-6; 4, 75700-29-7; 5, 75700-30-0.

A New Synthesis of Cyanohydrin Esters

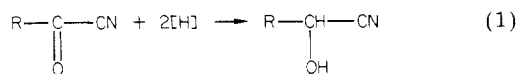
James M. Photis

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Received June 5, 1980

Cyanohydrins are commonly obtained by reaction of aldehydes and ketones with hydrogen cyanide.¹ Cyanohydrin esters are obtained by acylation of cyanohydrins which are often generated *in situ*² or by reaction of carbonyl compounds with specialized cyanation reagents.³ We have investigated the possibility of reduction of the

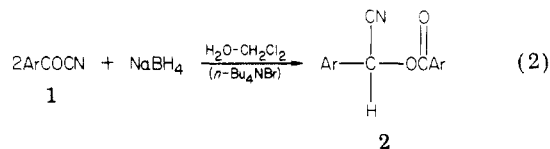
carbonyl group of acyl cyanides⁴ (reaction 1) as an alter-



native route to aldehyde-derived cyanohydrin intermediates. The starting material for this sequence is the corresponding carboxylic acid since acyl cyanides can be obtained from acid chlorides⁵ or anhydrides.⁶ Thus, this would be a more versatile synthetic route since an aromatic carboxylic acid is often more readily available than the corresponding aldehyde. Cyanohydrin esters are used commercially as potent insecticides.⁷

Catalytic hydrogenation of benzoyl cyanide⁸ proceeds with reduction of the nitrile functionality. The reaction of lithium aluminum hydride with benzoyl cyanide is reported⁹ to give complete reduction to 2-amino-1-phenylethanol. The sodium borohydride reduction of acyl cyanides is not known; however, it is known that borohydride does not react with the cyano functionality of ordinary nitriles¹⁰ unless the reagent is chemically modified.¹¹ The use of alcoholic solvents was avoided because acyl cyanides decompose in such solvents to give benzoates.¹² Phase-transfer-catalyzed (PTC) borohydride reactions of carbonyl compounds in H₂O-ClCH₂CH₂Cl have been reported,¹³ and this method appears to be reasonable because acyl cyanides have been shown to be stable to PTC conditions.¹⁴

An acyl cyanide (1) in CH₂Cl₂ was treated with a solution of NaBH₄ in water in the presence of tetra-*n*-butylammonium bromide catalyst (reaction 2). An exothermic



a, Ar = C₆H₅; b, Ar = *m*-C₆H₄CH₃; c, Ar = *p*-C₆H₄CH₃

reaction occurred and the acyl cyanide was completely consumed in just a few minutes. Removal and concentration of the CH₂Cl₂ layer produced an orange oil. The spectral data were identical with those reported¹⁵ for a cyanohydrin ester structure, 2, rather than a cyanohydrin. The yield was quantitative. Conversion of an acyl cyanide to a cyanohydrin ester is not without precedent. The low-temperature reaction of benzoyl cyanide with Grignard

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