plings in high yield, suggesting that further work is necessary in this field to achieve selective reductive couplings in the presence of other reducible functional groups.

Experimental Section

General Procedures. All melting and boiling points are uncorrected. Proton NMR spectra were run with a Varian CFT-20 using Me_4Si as the internal standard. Mass spectra were recorded with a Kratos MS-25 instrument. IR spectra were recorded with a PYE UNICAM 1100 spectrometer and UV spectra with a PYE UNICAM 1700.

Starting acetates and tosylates were prepared by treatment with Ac_2O and TsCl, respectively, in dry pyridine of the corresponding commercial phenols. Compound **2h** was synthesized from 5-formylsalicylic acid[15] by treatment with diazomethane. The synthesis of benzaldehyde **2i** is described below. The Zn–Cu couple was prepared according to the procedure of McMurry et al.[6a] All sensitive materials were transferred under inert atmosphere conditions, using a dry box or Schlenk apparatus. Solvents were dried by reflux over Na or H_2Ca in an Ar atmosphere. All starting materials were purified by crystallization or distillation under low pressure.

Benzaldehyde 2i. 3-Hydroxy-4-methoxybenzaldehyde (2 g, 13.1 mmol), succinic anhydride (1.986 g, 19.8 mmol), and 4-(dimethylamino)pyridine (32 mg, 0.26 mmol) were dissolved in 10 mL of dry pyridine and left for 2 days at room temperature. After addition of 30 mL of CH_2Cl_2, the resulting solution was washed 4 times with HCl (10%), dried (Na_2SO_4), and concentrated to half its volume by gently warming at the rotary evaporator. The solution was then immediately cooled in an ice bath and an ether solution of diazomethane (excess) was added. After 20 min unreacted diazomethane was destroyed with acetic acid, and the solution was washed with NaOH (5%), dried (Na_2SO_4), and concentrated under reduced pressure, giving compound **2i** as a thick oil (2.5 g, 72% yield). Distillation in a Kugelrohr oven in vacuo produced an analytically pure sample of compound **2i**: bp 190–5 °C (2 mm); IR (film) 1745, 1695, 1605, 1275 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 271 (3.83); ^1H NMR ($CDCl_3$) δ 7.72 (dd, J = 1.7 and 8.1 Hz, 1, 6-H), 7.56 (d, J = 1.7 Hz, 1, 2-H), 7.02 (d, J = 8.1 Hz, 1, 5-H), 3.90 and 3.72 (two 3 H singlets, $\mathbf{CH_3}O_2C$ and $\mathbf{CH_3}OAr$), and 2.73 (A_2B_2 system, 4, $RO_2C\mathbf{CH_2}\mathbf{CH_2}CO_2Ar$); mass spectrum, *m/e* 266 (M^+, 2), 235 (5), 152 (23), 151 (20), 116 (100).

Anal. Calcd for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30. Found: C, 58.77; H, 5.47.

General Procedure for the Titanium-Induced Couplings. $TiCl_3$ (1.03 g, 6.7 mmol) and 1.5 g of Zn–Cu couple[6a] were covered with 20 mL of dry solvent (see Table I). The mixture was refluxed for 1 h with effective stirring under Ar atmosphere. A solution of 3.35 mol of the carbonyl compound in 5 mL of dry solvent was added at once, and refluxing was continued for the amount of time indicated in Table I.

To the reaction mixture was added 25 g of silica gel, and the solvent was removed under vacuum, the residue being incorporated at the top of a silica gel column. Stilbenes were eluted with CH_2Cl_2, normally giving crystalline compounds.

Acknowledgment. To the Comisión Asesora de Investigatión Científica y Técnica (Spain) for its financial support, to INAPE for a grant to G.T., and to Professor M. Gayoso (Inorganic Department) (Santiago) for technical assistance.

Registry No. 2b, 881-57-2; **2c**, 34231-78-2; **2d**, 878-00-2; **2e**, 881-68-5; **2f**, 18749-47-8; **2g**, 7398-52-9; **2h**, 78515-16-9; **2i**, 78515-17-0; (*E*)-**3b**, 78515-18-1; (*E*)-**3c**, 78515-19-2; (*E*)-**3d**, 47241-75-8; (*E*)-**3e**, 7329-59-1; **3f**, 78515-20-5; **3g**, 78515-21-6; (*E*)-**3h**, 78515-22-7; (*E*)-**3i**, 78515-23-8; **4a**, 7150-01-8; **4b**, 7250-94-4; **5a**, 78515-24-9; **5b**, 7740-04-7; **5c**, 70188-11-3; (*E*)-**6a**, 78515-25-0; (*E*)-**6b**, 78515-26-1; **6c**, 78515-27-2; 3-hydroxy-4-methoxybenzaldehyde, 621-59-0; succinic anhydride, 108-30-5; Ti, 7440-32-6.

Supplementary Material Available: Table II, reporting the physical properties of compounds **3b,c,f,h,i** and **6a–c** (1 page). Ordering information is given on any current masthead page.

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Measurement and Estimation of the Heats of Vaporization of Hydrocarbons

James S. Chickos,*[1] Arthur S. Hyman,[2] Liina H. Ladon,[2,3] and Joel F. Liebman*[2]

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121, and the Department of Chemistry, University of Maryland Baltimore County, Catonsville, Maryland 21228

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Studies of the strain and resonance energies of organic compounds involve the heats of formation of the given species and that of the reference species to which it is compared.[4] Thermochemical logic suggests consideration of the ideal gas phase at STP as the standard reference state for comparison. The absence of the required ΔH_f and/or ΔH_v or ΔH_s has seemingly hindered many studies. For a given compound, the energy (enthalpy) of the condensed and gaseous phases are related by the heats of vaporization (ΔH_v) and sublimation (ΔH_s). Determination of these heats is often achieved by measuring the equilibrium vapor pressure of the compound at various temperatures. Direct measurement of vapor pressure has been used for both volatile solids and liquid. The measurement of low vapor pressures has been accomplished by a variety of methods.[5] Accurate measurement of low vapor pressures is more difficult and/or tedious, and the presence of systematic errors and disagreement between alternative approaches has rendered many of the reported results subject to question. Recently we reported on an equilibration technique which affords reliable ΔH_s results by measurement of vapor pressure as a function of temperature.[5] All previous results were obtained on solids of low volatility. We now report results which extend the range of this technique to liquid hydrocarbons of low to moderate volatility. We also elaborate on a simple empirical procedure for estimating heats of vaporization in instances where insufficient data are available in the literature.

The applicability of the equilibration technique to liquids of moderate volatility was demonstrated by comparison to vapor pressures obtained directly as a function of temperature. Four hydrocarbons were studied: 1-hexyne, 1-octene, phenylacetylene, and mesitylene. Direct measurement of vapor pressures was achieved by allowing a degassed sample to equilibrate with its vapor at a constant temperature. The vapor pressure was measured directly on a mercury manometer by using a cathetometer. A minimum of 5 min was allowed for each temperature equilibration. Null readings following each measurement were obtained by condensing the sample at −178 °C. Generally the vapor pressure measured at each temperature was obtained in triplicate.

Vapor pressure measurements by equilibration were obtained by slightly modifying the collection tube used previously.[5,6] The collection tube consisted of a U-shaped tube to which vacuum Teflon stopcocks had been attached at each end. The collection tube was attached to the apparatus and vacuum line by using O-ring seals. The

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[1] University of Missouri–St. Louis.

[2] University of Maryland Baltimore County.

[3] Department of Chemistry, Towson State University, Towson, MD.

[4] See, For example: Benson, S. W. "Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters", 2nd ed.; Wiley: New York, 1976. Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

[5] Chickos, J. S. *J. Chem. Educ.* **1975**, *52*, 134.

[6] Sandman, D. J.; Epstein, A. J.; Chickos, J. S.; Ketchum, J.; Fu, J. S.; Scheraga, H. A. *J. Chem. Phys.* **1979**, *70*, 305.

Table I. Heats of Vaporization

compd[b]	method[a]	ΔH_v[c]	ln A	r (n)	temp, °C	$\Delta H_v^{\text{lit.}\,c}$
1-hexyne	D	8.0	11.7	0.9998 (12)	−23 → +17	
	E	8.17	12.1	0.9995 (13)	−36 → +14	
1-octene	D	9.6	12.5	0.9993 (10)	−10 → +18	9.70[11]
	E	9.85	12.9	0.9998 (12)	−13 → +18	
phenylacetylene	D	10.5	12.9	0.9979 (13)	−8 → +18	10.5[12]
	E	10.8	13.5	0.9989 (7)	−3 → +19	
mesitylene	E	11.4	13.5	0.9998 (7)	0 → 26	11.35[11]

[a] Heats of vaporization; where D denotes direct measurement and E denotes measurement by sample equilibration.[5] [b] 1-Hexyne and 1-octene used were analyzed by gas chromatography and found to be 99+% pure. Phenylacetylene (98%, Aldrich Chemical Co.) was used without further purification. [c] In kcal mol^{-1}.

Table II. Comparison of Experimental and Estimated ΔH_v (kcal mol^{-1})

compd	ΔH_v (exptl)	ΔH_v (eq) 1	2	3	4
1-hexyne	8.0, 8.17	7.4 ± 0.3	7.4 ± 0.2	7.5 ± 0.2	7.5 ± 0.4
1-octene	9.6, 9.85	9.5 ± 0.3	9.7 ± 0.2	9.7 ± 0.2	9.8 ± 0.6
phenylacetylene	10.5, 10.8	9.6 ± 0.3	9.7 ± 0.2	9.7 ± 0.2	9.8 ± 0.6
mesitylene	11.4	10.7 ± 0.3	10.8 ± 0.2	10.8 ± 0.2	10.9 ± 0.6

typical procedure used for each run included sample equilibration with the 3-L ballast tank for a minimum of 15 min and transfer and condensation of the vapor at −178 °C in the U-tube. A period of 10 min was allowed for the latter process. The stopcocks were then closed, and the collection tube was removed from the apparatus. The collection tube was warmed up to room temperature and weighed to constant weight. The tube was next attached to a vacuum line and the sample transfered. The evacuated collection tube was reweighed and the sample size determined by difference. The tare weight of the collection tube was reproduced between consecutive runs within a few tenths of a milligram. Sample sizes ranged from 400 to 20 mg. Most measurements at each temperature were performed in triplicate. Constant-temperature baths were obtained by using the solid–liquid equilibrium of appropriate substances. Temperatures were monitored by using a Chromel-Alumel thermocouple attached to the exterior of the sample compartment of the apparatus. Temperatures are believed accurate to ±0.2 °C except for the lowest temperatures which are believed good to ±0.5 °C. The ballast tank was kept at 76 °C for all measurements.

Analysis of the data was carried out as follows. Heats of vaporization (kcal/mol) were calculated by a linear, least-squares fit of the imput data. The results are included in Table I for both methods along with the correlation coefficient (*r*), the number of imput data points (*n*), the temperature range studied, and the literature value when available. Comparison of the vapor pressures obtained over the temperature range studied shows good agreement between the two methods, generally within 5%. Heats of vaporization agree within 3%, and comparison with the literature values is equally good. We therefore conclude that the equilibration technique described in this and previous reports[5,6] can be used reliably in the pressure range 10^{-6}–10^{-1} atm for solids and liquid hydrocarbons. In addition, we have no experimental reason for believing that this range cannot be expanded to higher pressures.

The observation that the ΔH_v of 1-octene and phenylacetylene are comparable and close to the value for other C_8 hydrocarbons[7] (e.g., octane, 9.9 kcal/mol; cyclooctane, 10.4 kcal/mol; ethylbenzene, 10.8 kcal/mol) suggests a simple estimation approach for the quantity of interest.[8] The simplest estimation procedure, linearity of ΔH_v with the number of carbons, n_C, provides a high degree of accuracy for the homologus series of *n*-alkanes and some of their 1-substituted derivatives.[9] Using 138 structurally diverse hydrocarbons of ref 7, for which accurate ΔH_f and ΔH_v data were available (V1-C1 data of ref. 7), we also find linearity (see eq 1). Inspection shows compounds with

$$\Delta H_v = (1.11 \pm 0.03)n_c + (0.70 \pm 0.19) \qquad (1)$$

$$r = 0.965,\ \sigma = 0.59$$

quarternary carbons have consistently lower ΔH_v values than those lacking this structural feature. A two-parameter fit with ΔH_v vs. the number of quarternary carbons, n_Q, and nonquaternaries, $\tilde{n}_C \equiv n_C - n_Q$, gives eq 2.

$$\Delta H_v = (0.31 \pm 0.05)n_Q + (1.12 \pm 0.02)\tilde{n}_C + (0.71 \pm 0.15) \qquad (2)$$

$$r = 0.994,\ \sigma = 0.40$$

Because the coefficient for n_Q is small and the coefficient of $\tilde{n}_C$ nearly equals n_C and the earlier literature value,[9] 1.12, a new one-parameter equation is given as eq 3. Since ΔH_v

$$\Delta H_v = (1.11 \pm 0.02)n_C + (0.85 \pm 0.15) \qquad (3)$$

$$r = 0.975,\ \sigma = 0.41$$

for a compound with no carbons would be expected to equal *RT* (nearly our intercept),[10] we obtain the simplest

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[7] All data in this paper, unless otherwise stated, is from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970, and refers to 298 K.

[8] We acknowledge the multiparameter approaches discussed in the following: (a) Cox, J. D.; Pilcher, G., ref 7, Chapter 4. (b) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. R. "Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1978; Chapter 6. (c) Cremer, R. D., III. *J. Am. Chem. Soc.* **1980**, *102*, 1837, 1849. (d) DuCros, M.; Gruson, J. F., Sannier, H. *Thermochim. Acta* **1980**, *36*, 39. However, the above near equality suggested that simpler approaches are feasible. In addition, the methods cited above depend on experimental or structural parameters not always available (e.g., critical properties[8a–c]). Other methods have not been extended to handle all hydrocarbon functionalities such as acetylenes.[8d]

[9] Mannson, M.; Sellers, P.; Stridh, G.; Sunner, S. *J. Chem. Thermodyn.* **1977**, *9*, 91.

[10] The reader may inquire whether a linear fit was artificially forced upon the estimation approach. To check this, we computed the best power by a least-squares fit of ln ($\Delta H_v - RT$) vs. ln ($\tilde{n}_C + 0.3n_Q$) (cf. eq 2). The calculated power is 0.968 (±0.019) with an associated $r = 0.975$. Linearity is suggested.

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equation (eq 4). Table II presents our "predictions" for

$$\Delta H_v = (1.15 \pm 0.07)n_C + RT \qquad (4)$$

$$\sigma = 0.70$$

the four hydrocarbons discussed earlier. Quick perusal shows the average discrepancy is ca. 0.6 kcal/mol. This quantity is small enough, that we feel this method can be useful in predicting ΔH_v in cases where experimental data do not exist.

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Registry No. 1-Hexyne, 693-02-7; 1-octene, 111-66-0; phenylacetylene, 501-65-5; mesitylene, 108-67-8; 1-butyne, 107-00-6; 2-butyne, 503-17-3; 1,2-butadiene, 590-19-2; 1,3-butadiene, 106-99-0; 1-butene, 106-98-9; (*Z*)-2-butene, 590-18-1; (*E*)-2-butene, 624-64-6; isobutene, 115-11-7; cyclobutane, 287-23-0; butane, 106-97-8; isobutane, 75-28-5; cyclopentene, 142-29-0; spiropentane, 157-40-4; pentene, 109-67-1; (*Z*)-2-pentene, 627-20-3; (*E*)–2–pentene, 646-04-8; 2-methyl-1-butene, 563-46-2; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; cyclopentane, 287-92-3; pentane, 109-66-0; 2-methylbutane, 78-78-4; benzene, 71-43-2; cyclohexene, 110-83-8; 1-hexene, 592-41-6; (*Z*)-2-hexene, 7688-21-3; (*E*)-2-hexene, 4050-45-7; (*Z*)-3-hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; 2-methyl-1-pentene, 763-29-1; 3-methyl-1-pentene, 760-20-3; 4-methyl-1-pentene, 691-37-2; 2-methyl-2-pentene, 625-27-4; (*Z*)-3-methyl-2-pentene, 922-62-3; *(E)-3-methyl-2-pentene*, 616-12-6; (*Z*)-4-methyl-2-pentene, 691-38-3; (*E*)-4-methyl-2-pentene, 674-76-0; 2-ethyl-1-butene, 760-21-4; 2,3-dimethyl-1-butene, 563-78-0; 3,3-dimethyl-1-butene, 558-37-2; 2,3-dimethyl-2-butene, 563-79-1; methylcyclopentane, 96-37-7; cyclohexane, 110-82-7; hexane, 110-54-3; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8; cycloheptatriene, 544-25-2; toluene, 108-88-3; 1-methylcyclohexene, 591-49-1; 1-heptene, 592-76-7; 4-methylheptane, 589-53-7; 3-ethylhexane, 619-99-8; 2,2-dimethylhexane, 590-73-8; 2,3-dimethylhexane, 584-94-1; 2,4-dimethylhexane, 589-43-5; 2,5-dimethylhexane, 592-13-2; 3,3-dimethylhexane, 563-16-6; 3,4-dimethylhexane, 583-48-2; 3-ethyl-2-methylpentane, 609-26-7; 3-ethyl-3-methylpentane, 1067-08-9; 2,2,3-trimethylpentane, 564-02-3; 2,2,4-trimethylpentane, 540-84-1; 2,3,3-trimethylpentane, 560-21-4; 2,3,4-trimethylpentane, 565-75-3; propylbenzene, 103-65-1; isopropylbenzene, 98-82-8; 1-methyl-2-ethylbenzene, 611-14-3; 1-methyl-3-ethylbenzene, 620-14-4; 1-methyl-4-ethylbenzene, 622-96-8; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8; propylcyclohexane, 1678-92-8; nonane, 111-84-2; butylbenzene, 104-51-8; *iso*-butylbenzene, 538-93-2; *sec*-butylbenzene, 135-98-8; *tert*-butylbenzene, 98-06-6; *cis*-decahydronaphthalene, 493-01-6; *trans*-decahydronaphthalene, 493-02-7; 1-decene, 872-05-9; butylcyclohexane, 1678-93-9; decane, 124-18-5; heptylcyclohexane, 5617-41-4; (*Z*)-3-methyl-3-hexene, 4914-89-0; (*E*)-3-methyl-3-hexene, 3899-36-3; 2,4-dimethyl-1-pentene, 2213-32-3; 4,4-dimethyl-1-pentene, 762-62-9; 2,4-dimethyl-2-pentene, 625-65-0; (*Z*)-4,4-dimethyl-2-pentene, 762-63-0; (*E*)-4,4-dimethyl-2-pentene, 690-08-4; 3-methyl-2-ethyl-1-butene, 7357-93-9; 2,3,3-trimethyl-1-butene, 594-56-9; 1,1-dimethylcyclopentane, 1638-26-2; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,2-dimethylcyclopentane, 822-50-4; *cis*-1,3-dimethylcyclopentane, 2532-58-3; *trans*-1,3-dimethylcyclopentane, 1759-58-6; ethylcyclopentane, 1640-89-7; methylcyclohexane, 108-87-2; cycloheptane, 291-64-5; heptane, 142-82-5; 2-methylhexane, 591-76-4; 3-methylhexane, 589-34-4; 3-ethylpentane, 617-78-7; 2,2-dimethylpentane, 590-35-2; 2,3-dimethylpentane, 565-59-3; 2,4-dimethylpentane, 108-08-7; 3,3-dimethylpentane, 562-49-2; 2,2,3-trimethylbutane, 464-06-2; 1,3,5,7-cyclooctatetraene, 629-20-9; styrene, 100-42-5; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1-ethylcyclohexene, 1453-24-3; (*Z*)-2,2-dimethyl-3-hexene, 690-92-6; (*E*)-2,2-dimethyl-3-hexene, 690-93-7; 2-methyl-3-ethyl-1-pentene, 19780-66-6; 2,4,4-trimethyl-1-pentene, 107-39-1; 2,4,4-trimethyl-2-pentene, 107-40-4; propylcyclopentane, 2040-96-2; ethylcyclohexane, 1678-91-7; 1,1-dimethylcyclohexane, 590-66-9; *cis*-1,2-dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,3-dimethylcyclohexane, 638-04-0; *trans*-1,3-dimethylcyclohexane, 2207-03-6; *cis*-1,4-dimethylcyclohexane, 624-29-3; *trans*-1,4-dimethylcyclohexane, 2207-04-7; cyclooctane, 292-64-8; octane, 111-65-9; 2-methylheptane, 592-27-8; 3-methylheptane, 589-81-1; isoprene, 78-79-5; indene, 95-13-6; 2,3-dihydroindene, 496-11-7; *cis*-bicyclo[4.3.0]nonane, 4551-51-3; *trans*-bicyclo[4.3.0]nonane, 3296-50-2; α-pinene, 80-56-8; β-pinene, 127-91-3; cyclopentadiene, 542-92-7; 1,2,3,4-tetrahydronaphthalene, 119-64-2; α-phellandrene, 99-83-2; *cis*-stilbene, 645-49-8; hexadecane, 544-76-3; dodecylcyclohexane, 1795-17-1; (+)-limonene, 5989-27-5; dipentene, 138-86-3; 6,6-dimethylfulvene, 2175-91-9; 1,1-diphenylethylene, 530-48-3; undecane, 1120-21-4; dodecane, 112-40-3; decylbenzene, 104-72-3; hexadecene, 629-73-2; 3,3-diethylpentane, 1067-20-5; 2,2,3,3-tetramethylpentane, 7154-79-2; 2,2,3,4-tetramethylpentane, 1186-53-4; 2,2,4,4-tetramethylpentane, 1070-87-7; 2,3,3,4-tetramethylpentane, 16747-38-9; 2-methylnonane, 871-83-0; 5-methylnonane, 15869-85-9; 2,2,5,5-tetramethylheptane, 61868-47-1; 2,2,4,4,5-petamethylhexane, 60302-23-0; 3,3,6,6-tetramethyloctane, 62199-46-6; 4,4,6,6-tetramethylnonane, 74286-93-4; 3,5-dimethyl-3,5-diethylheptane, 74286-94-5; 5,5,7,7-tetramethylundecane, 74286-95-6; 5-butyldocosane, 55282-16-1; 11-butyldocosane, 13475-76-8; 11-decylheneicosane, 55320-06-4; bicyclopropyl, 5685-46-1; cyclodecane, 293-96-9; cycloundecane, 294-41-7; cyclotridecane, 295-02-3; 1-methylcyclopentene, 693-89-0; 3-methylcyclopentene, 1120-62-3; 4-methylcyclopentene, 1759-81-5.

Supplementary Material Available: Tables containing the names and heats of vaporization of the 138 compounds used to derive eq 1–4 and a comparison of the predicted and experimental values for an additonal 44 compounds (5 pages). Ordering information is given on any current masthead page.

A Convenient Synthesis of Alkyl Amines via the Reaction of Organoboranes with Ammonium Hydroxide

George W. Kabalka,* Kunda A. R. Sastry,
Gary W. McCollum, and Hiroaki Yoshioka

Chemistry Department, University of Tennessee, Knoxville, Tennessee 37916

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The synthesis of amines has long been of interest due to their physiological activity and their potential as organic intermediates. Brown reported that organoboranes could be utilized to produce amines by treating them with chloramine[1] or hydroxylamine-*O*-sulfonic acid.[2] The reactions involve the regiospecific replacement of the boron atom by the amino group. These reactions have not been utilized extensively, presumably due to the cumbersome preparation and inherent instability of chloramine[3] and the expense of hydroxylamine-*O*-sulfonic acid.

$$R_3B \xrightarrow{NH_2Cl} RNH_2$$

In recent years, we have had success in carrying out reactions in systems where the reagents are generated in situ.[4,5] For example, organoboranes will react with iodide

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