(75 mmol, 3 mL) was introduced, and buta-1,3-diene (300 mmol, 16.2 g) was distilled into the autoclave cooled at -20 °C. Heating for 20 h at 80 °C gave rise to a total conversion of butadiene. GC and GC-MS analysis of the crude reaction mixture revealed the formation of small amounts of butadiene dimers (4-vinylcyclohexene, octa-1,3,6- and -1,3,7-triene) (2%), C_8 telomers (m/z = 140) (20%), a small amount of a C_{12} telomer (m/z = 194) (1%), a small amount of a butadiene tetramer (m/z = 216) (3%), and C_{16} telomers (m/z = 248) (34%) together with some higher oligomers and telomers. Distillation of the reaction mixture afforded a low-boiling fraction (bp 50–55 °C, 1 Torr) and a high-boiling fraction (bp 50–60 °C, 10^{-2} Torr).

The low-boiling fraction consisted of a mixture of **1** (90%) and **2** (10%), which were identified by comparison of their GC retention time and spectral data (^{1}H NMR, MS) with those of authentic samples.[41]

The high-boiling fraction was analyzed by GC and GC-MS and found to be a mixture of a butadiene tetramer (m/z = 216) (5%) and two C_{16} telomers (m/z = 248) **3** (8%) and **4** (87%). Distillation of this fraction gave pure compound **4**, which presented the following spectroscopic properties: IR (neat) 1640, 1100, 990, 970, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (m, 4 H, CH_2), 1.8–2.3 (m, 10 H, allylic), 3.3 (s, 3 H, CH_3), 3.55 (q, 1 H, C*H*O, J = 6 Hz), 4.9–6.0 (m, 10 H, *H*C=); mass spectrum, m/z (relative intensity) 248 (M^+, 0.4), 216 (M^+ - MeOH, 0.6), 107 (43), 79 (86), 71 (100), 67 (61), 41 (64).

Hydrogenation of compound **4** over Adams platinum gave quantitatively 3-methoxyhexadecane, which was identical (IR, ^{1}H NMR, MS, GC retention time) with an authentic sample prepared from commercial 3-hexadecanol.

From these data, compound **4** is 3-methoxyhexadeca-1,6-(7),10(11),15-tetraene. However, the characterization of **4** as 3-methoxyhexadeca-1,6,10,15-tetraene is favored on the basis of mechanistic studies.[42]

Column chromatography of a sample of the high-boiling fraction on silica gel eluting with 5% ethyl acetate in cyclohexane afforded a mixture of compounds **3** and **4** (1/3). ^{1}H NMR spectroscopy showed the resonances of compound **4** and resonances as δ 3.25 (s, 3 H, CH_3) and 3.80 (d, 2 H, CH_2O, J = 4 Hz). Hydrogenation of this mixture quantitatively furnished a mixture of 1-methoxyhexadecane and 3-methoxyhexadecane, identified by comparison (GC retention time) with authentic samples prepared from commercial 1- and 3-hexadecanol, respectively. From these data, compound **3** is a 1-methoxyhexadeca-3,x,x,x,-tetraene.

Alternatively, the methoxyoctadienes were synthesized as follows.

Preparation of 1-Methoxyocta-2,7-diene (1) and 3-Methoxyocta-1,7-diene (2). $Pd(dba)_2$ (0.3 mmol, 172 mg) and PPh_3 (0.6 mmol, 157 mg) were weighed in a 300-mL autoclave under argon. Methanol (90 mL) was introduced, and buta-1,3-diene (90 mL, 55 g, 1 mol) was distilled into the autoclave cooled to -20 °C. After heating at 80 °C for 20 h and cooling, the reaction products were submitted to distillation to afford 63 g (90%) of a mixture of **1** (97%) and **2** (3%), bp 62–68 °C (13 Torr), whose spectral data are in agreement with the reported values.[41]

Procedure for the Carbonylation Reaction. The catalyst precursor was weighed in a 100-mL autoclave under argon. A solution of the C_8 fraction (50 mmol, 7 g) or of the C_{16} fraction (20 mmol, 5 g) was introduced, and the autoclave was pressurized with carbon monoxide and heated to the temperature reported in Table I. After the desired reaction time, the products were analyzed by GC or isolated through distillation.

Methyl Nona-3,8-dienoate (5). Distillation of the products of experiment 14 afforded 5.88 g (70%) of methyl nona-3,8-dienoate, bp 90–100 °C (17–18 Torr), which was identical (IR, ^{1}H NMR, GC) with an authentic sample prepared according to ref 43.

Methyl Heptadeca-3,7,11,16-tetraenoate (7). Distillation of the reaction products afforded 2.78 g (50%) of methyl heptadeca-3,7,11,16-tetraenoate, bp 120–124 °C (1 Torr), which presented the following spectroscopic properties: IR (neat) 1740, 1640, 990, 970, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (m, 2 H, CH_2), 1.8–2.3 (m, 12 H, allylic), 3.05 (m, 2 H, CH_2CO_2Me), 3.7 (s, 3 H, CH_3), 4.8–5.1 (m, 2 H, =CH_2), 5.3–5.8 (m, 7 H, *H*C=C*H*).

Hydrogenation of 5 and 7. A solution of compound **5** or **7** (0.5 mmol) in hexane (4 mL) was introduced in a 100-mL autoclave containing Adams platinum (20 mg). The autoclave was pressurized with hydrogen (30 atm) and heated to 50 °C for 4 h. After filtration of the cooled solution through Celite and evaporation of the solvent, a quantitative yield of methyl pelargonate or methyl margarate was obtained. Their IR and ^{1}H NMR spectra and their GC retention times were identical with those of commercial products (Fluka).

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Registry No. **1**, 35702-75-1; **2**, 20202-62-4; **3**, 119595-27-6; **4**, 119595-28-7; **5**, 51122-98-6; **7**, 119595-29-8; $Pd(dba)_2$, 81141-80-2; $[(\eta^3$-methyl-2-allyl)$PdCl]_2$, 12081-18-4; [(2-methylallyl)oxy]tris(dimethylamino)phosphonium hexafluorophosphate, 63936-88-9; buta-1,3-diene, 106-99-0; methyl pelargonate, 1731-84-6; methyl margarate, 1731-92-6.

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1-Silacyclohexan-4-ones and 1-Germacyclohexan-4-ones: Precursors to Metallapharmaceuticals via Boracycles

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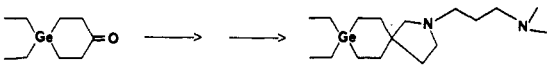
The pioneering studies of Rice and co-workers[2] established that 1-metallacyclohexan-4-ones could be efficiently converted to the pharmacologically important 2-aza-8-metallaspiro[4.5]decanes. "Spirogermanium" (**2**), for example, is reported to have antitumor, antiarthritic, antimalarial, and immunoregulatory activity[3] and is available in several steps from 1,1-diethyl-1-germacyclohexan-4-one (**1d**).[2a]



(eq. 1)

1d **2**

For some time, we have had an interest in the preparation and chemistry of such metallacyclohexan-4-one systems (**1**).[4] After finding the reported methods to this and other ring systems to involve many steps and give low overall yields,[2,5] we took advantage of several newer organoborane-based routes to cyclic ketones and applied

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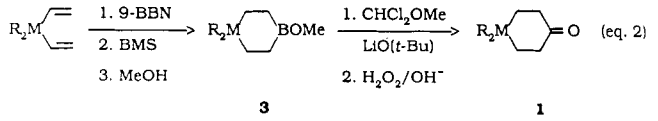
0022-3263/89/1954-2462$01.50/0

Table I. Divinylsilanes and -germanes to Metallacyclohexanones

series	yield, % 3	1
a (Me_2Si)	76	88
c (Et_2Si)	78	75
d (Et_2Ge)	73	91
e (Pr_2Ge)	76	88

these methods to the syntheses of 1 and larger ring metallacyclanones.[4] For 1, we found that the initial hydroboration of the divinyl compounds with 9-borabicyclo[3.3.1]nonane (9-BBN) gave the necessary 1,5-diboryl relationship, and the regiospecific exchange of these adducts with borane–dimethyl sulfide complex (BMS) gave isolable metallaborinanes (3). These boracycles were converted, with Brown's DCME process,[6] to the desired ketone products, 1. In this paper, we report modifications of our original procedures, which significantly improve the overall process. Also, through the selection of additional examples with differing alkyl substitution on the metalloid, the scope of the process has been significantly expanded to include several new systems (eq 2) (cf. Table I).



3 1

Several aspects of these modifications and additions are noteworthy. First, the preparation and isolation of the intermediate borinanes, 3, can now be efficiently carried out in a one-pot reaction. The byproduct, 4, can be conveniently recycled back to 9-BBN in >90% yield by our recently reported method.[8] This avoids the necessity to selectively crystallize a portion of the 9-BBN prior to the methanolysis of the mixture, a drawback of our original procedures.[4b] Essentially identical yields of **3a** were obtained for both methods, the present approach being much simpler in an operational sense. Second, we have now established through the preparation of the diethyl- and dipropylgermanium derivatives (i.e. **3d,e**) that the procedure is highly useful for the preparation of germa- as well as silaborinanes. Thus, both lower (e.g. **3a**) and higher (e.g. **3c–e**) boiling heterocycles, compared to 4, can be prepared and isolated in pure form. If the boracycle cannot be separated from *B*-MeO-9-BBN (4) because of their similar boiling points (e.g. **3b** (R_2M = Me_2Ge)), the approach can be further modified to give the desired ketone product, but in lower yield.[4b] For the **3** → **1** conversion, we investigated many conditions, finding that LiO(*t*-Bu) (5 equiv) could be substituted for the standard $LiOCEt_3$ base (2 equiv).[4,6] For **1a**, this change increased the yield from 67% to 88%.[7] For the other examples, excellent yields were also obtained (cf. Table I). This modification becomes particularly significant for the germanium heterocycles where the starting compounds are far more expensive than for the silanes. Also, *tert*-butyl alcohol is far easier to separate from the products than is triethylcarbinol. Moreover, the reaction is much cleaner with these new conditions, because the diol byproducts that are derived from unconverted **3** with our older process are essentially eliminated with this new procedure. Consequently, the distillative isolation of 1 is also now much simpler and no longer requires the use of special equipment.

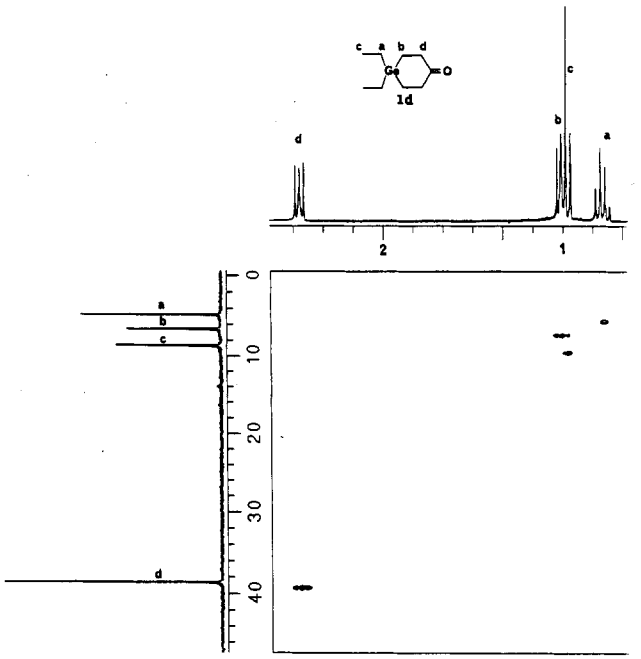


Figure 1. HETCOR spectrum of 1,1-diethyl-1-germacyclohexan-4-one.

Traditionally, heterocyclic compounds such as 1 and 3 have been extremely difficult to fully characterize by NMR due to the overlapping absorbances or nearly coincident signals. With 1,1-dimethyl-1-metalla systems, we have expended much time and energy in the past, to add to the very limited spectroscopic information available for these rare systems.[4] However, in the present study, the diethyl and dipropyl systems proved to be too complex, for any meaningful analysis with low-field, 1D NMR data. Thus, we carried out a detailed investigation of the present systems employing 300-MHz NMR together with DEPT and HETCOR NMR experiments to assign the ^1H and ^{13}C NMR spectra for these compounds (see the Experimental Section). For **1d**, this latter experiment is presented in Figure 1. It can be noted that the α-metalloidal exocyclic methylenes are upfield from their ring counterparts (or β-methyl groups) in each case in both the ^1H and ^{13}C NMR spectra of these diethyl derivatives. For the dipropyl compounds (i.e. **1e**, **3e**), the opposite is true, making such experiments invaluable for precise assignments in such heterocycles.

In this work, we have presented a new, improved methodology for the preparation of 1-sila- or 1-germacyclohexan-4-ones, which, in an operationally simple manner, gives the desired heterocycles in excellent yields and chemical purity.

Experimental Section

All experiments were carried out in predried (12 h at 125 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[4,9] Analytical gas chromatography was performed with either a Perkin-Elmer Sigma-1B GC equipped with a 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS treated Chromasorb W packed column

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(7) We wish to point out that our previous yield for **3a** to **1a** was reported[4b] to be 67%. This value is correct, but the gram amount given corresponded to a 100-mmol scale reaction and not the 160-mmol scale described. Our new methodology is much better, giving 88% of **1a** from **3a**.

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or a Perkin-Elmer 8320 capillary gas chromatograph with a 30 m × 0.25 mm bonded FSOT 20% SE-30 capillary column. Spectra were recorded on the following instruments: IR: Perkin-Elmer 283 spectrometer or Nicolet 6000 series FT-IR (TF = thin film). MS: Hewlett-Packard 5995 GC/MS (70 eV) (For both series d and e, only ^{74}Ge peaks are reported). NMR: GE Models QE and GN 300-MHz NMR spectrometers (^{1}H and ^{13}C (Me_4Si: δ = 0.00 ppm), ^{11}B (BF_3–OEt_2: δ 0.0 ppm)). All solvents and reagents were purified prior to use by standard methods (cf. ref 4b).

1,1-Dimethyl-4-methoxy-1-sila-4-borinane (3a). To a mixture of 9-BBN (63.6 g, 0.52 mol) in dry hexanes (625 mL) was added divinyldimethylsilane (29.1 g, 0.26 mol). The stirred mixture was heated at reflux temperature for 2 h. After the mixture was cooled to room temperature, BMS (27.5 mL, 9.45 M; 0.26 mol) was added, followed by heating at reflux for 2 h. After the reaction mixture was cooled to room temperature, MeOH (62.5 mL) was added dropwise (H_2 evolution). The solvents were removed by distillation under a nitrogen atmosphere. Vacuum distillation of the residue provided 30.7 g (76%) of **3a** (bp 21–3 °C, 0.15 Torr) and 71.3 g (90%) of **4** (bp 32–3 °C, 0.15 Torr). For **3a**, the physical and spectroscopic properties were identical with previous values.[4b]

1,1-Diethyl-4-methoxy-1-sila-4-borinane (3c). From 9-BBN (5.0 g, 41 mmol) in dry hexanes (50 mL) and divinyldiethylsilane (2.87 g, 20.5 mmol), as for **3a** [BMS (2.05 mL, 9.98 M; 20.5 mmol); MeOH (4 mL)], distillation afforded 5.13 g (80%) of **4** and 2.95 g (78%) of pure **3c** (bp 47–9 °C, 0.2 Torr). ^{11}B NMR ($CDCl_3$): δ 52.3 ppm. ^{13}C NMR ($CDCl_3$): δ 3.8 (CH_2CH_3), 4.5 ($SiCH_2CH_2$), 7.3 (CH_2CH_3), 12.9 (b, CH_2CH_2B), 52.8 (OCH_3) ppm. ^{1}H NMR δ 0.51 (q, 4 H, J = 8 Hz), 0.61 (ct, 4 H), 0.93 (t, 6 H), J = 8 Hz), 0.97 (ct, 4 H), 3.63 (s, 3 H) ppm. MS: m/z 184 (M^+, 53), 170 (22), 156 (51), 155 (100), 141 (39), 127 (45), 113 (55); 111 (35); 85 (56); 59 (42); 57 (22).

1,1-Diethyl-4-methoxy-1-germa-4-borinane (3d). From 9-BBN (73.3 g, 0.600 mol) in dry hexanes (700 mL) and divinyldiethylgermane (55.4 g, 0.300 mol), as for **3a** [BMS (33.1 mL, 9.04 M; 0.300 mol); MeOH (37 mL)], distillation provided 80 g (85%) of **4** (bp 47–9 °C, 1.5 Torr) and 50.2 g (73%) of pure **3d** (bp 68–70 °C, 1.2 Torr). ^{11}B NMR ($CDCl_3$): δ 55.6 ppm. ^{13}C NMR ($CDCl_3$): δ 4.0 (CH_2CH_3), 5.3 ($GeCH_2CH_2$), 8.9 (CH_2CH_3), 14.6 (b, CH_2CH_2B), 52.8 (OCH_3) ppm. ^{1}H NMR δ 0.73 (q, 4 H, J = 8 Hz), 0.83 (t, 4 H), J = 7.2 Hz), 1.03 (t, 6 H, J = 8 Hz), 1.06 (t, 4 H), J = 7.2 Hz), 3.61 (s, 3 H) ppm. MS: m/z 230 (M^+ (Ge - 74), 11), 201 (M - Et, 100), 173 (36), 157 (41), 145 (38), 131 (31), 103 (84), 75 (36).

1,1-Dipropyl-4-methoxy-1-germa-4-borinane (3e). From 9-BBN (5.47 g, 44.9 mmol) in dry hexanes (50 mL) and divinyldipropylgermane (4.77 g, 22.4 mmol), as for **3a** [BMS (2.5 mL, 9.00 M; 22.4 mmol); MeOH (4 mL)], distillation provided 5.9 g (84%) of **4** and 4.30 g (76%) of pure **3e** (bp 95–7 °C, 0.2 Torr). ^{11}B NMR ($CDCl_3$): δ 52.5 ppm. ^{13}C NMR ($CDCl_3$): δ 5.2 ($GeCH_2CH_2B$), 14.7 (b, CH_2CH_2B), 16.6 (CH_2Et), 18.0 ($CH_2CH_2CH_3$), 18.9 ($CH_2CH_2CH_3$), 52.8 (OCH_3) ppm. ^{1}H NMR δ 0.74 (m, 4 H), 0.82 (ct, 4 H), 0.94 (t, 6 H), J = 7.2 Hz), 1.05 (ct, 4 H), 1.43 (m, 4 H), 3.62 (s, 3 H) ppm. MS: m/z (51), 147 (100), 105 (76).

1,1-Dimethyl-1-silacyclohexan-4-one (1a). To a stirred solution of **3a** (6.5 g, 42 mmol) and dichloromethyl methyl ether (DCME) (5.02 g, 42 mmol) in THF (250 mL) at 0 °C was added, via a double-ended needle, lithium *tert*-butoxide solution (from 81 mL, 2.58 M Li(*n*-Bu) and *tert*-butyl alcohol (20 mL, 208 mmol)). After 10 min, the mixture was allowed to warm to room temperature and after 30 min, ethanol (35 mL 95%), water (10 mL), and NaOH pellets (5.0 g, 125 mg-atom) were added followed by the dropwise addition of 35% hydrogen peroxide (14 mL). After the addition was complete, the mixture was heated at reflux temperature for 1.5 h, allowed to cool to room temperature, and extracted with saturated brine (80 mL). The organic layer was dried (K_2CO_3), concentrated at reduced pressure, and distilled at 59 Torr to give 5.2 g (88%) of **1a** (bp 118–120 °C). For **1a**, the physical and spectroscopic properties were identical with previous values.[1a,4b,7]

1,1-Diethyl-1-silacyclohexan-4-one (1c). From **3c** (2.66 g, 14.4 mmol), DCME (1.66 g, 14.4 mmol) in THF (90 mL) and LiO(*t*-Bu) solution (from 40 mL, 1.82 M Li(*t*-Bu) and *t*-BuOH (3.8 mL, 72 mmol)), as for **1a** [ethanol (12 mL, 95%), water (3 mL), NaOH pellets (2.0 g, 50 mg-atom), 35% hydrogen peroxide (5.0 mL), saturated brine (35 mL)], distillation gave 1.85 g (75%) of **1c** (bp 67–70 °C, 0.4 Torr). Anal. Calcd for $C_9H_{18}SiO$: C, 63.47; H, 10.65. Found: C, 63.21; H, 10.64. ^{13}C NMR ($CDCl_3$): δ 3.9 (CH_2CH_3), 6.6 ($SiCH_2CH_2$), 7.3 (CH_2CH_3), 37.8 ($SiCH_2CH_2$), 214.9 (C=O) ppm. ^{1}H NMR δ 0.66 (q, 4 H, J = 7.8 Hz), 0.93 (ct, 4 H), 1.00 (t, 6 H, J = 7.8 Hz), 2.50 (ct, 4 H) ppm. IR (TF): 1708 cm^{-1}. MS: m/z 170 (M^+, 19, 142 (M - C_2H_4, 40), 141 (M - Et, 57), 114 (142 - CO, 55), 113 (141 - C_2H_4, 100, 87 (22), 86 (72), 85 (53), 75 (31), 59 (22), 58 (70), 57 (89), 56 (37), 55 (59), 53 (21).

1,1-Diethyl-1-germacyclohexan-4-one (1d). From **3d** (50.2 g, 218 mmol), DCME (25.0 g, 218 mmol) in THF (1.3 L), and LiO(*t*-Bu) solution (from 570 mL, 1.80 M Li(*t*-Bu) and *t*-BuOH (97 mL, 1.03 mol)), as for **1a** [ethanol (175 mL 95), water (46 mL), and NaOH pellets (27 g, 0.68 g-atom), 35% hydrogen peroxide (72 mL), saturated brine (500 mL)], distillation at 0.4 Torr gave 42.6 g (91%) of **1d** [bp 72–4 °C (lit.[2b] bp 84–5 °C, 1.5 Torr)]. Anal. Calcd for $C_9H_{18}GeO$: C, 50.32; H, 8.44. Found: C, 50.39; H, 8.47. ^{13}C NMR ($CDCl_3$): δ 4.5 (CH_2CH_3), 6.4 ($GeCH_2CH_2$), 8.3 (CH_2CH_3), 38.2 ($GeCH_2CH_2$), 213.4 (C=O) ppm. ^{1}H NMR δ 0.62 (cq, 4 H, J = 8 Hz (calcd), 0.82 (t, 6 H, J = 8 Hz (calcd), 0.85 (ct, 4 H), 2.29 (ct, 4 H) ppm. IR (TF): 1705 cm^{-1}, MS: m/z 216 (M^+, 32, 187 (M - Et, 55), 159 (187 - C_2H_4, 37), 131 (159 - CO, 51), 103 (GeC_2H_5, 100).

1,1-Dipropyl-1-germacyclohexan-4-one (1e). From **3e** (1.96 g, 7.6 mmol), DCME (0.89 g, 7.6 mmol) in THF (45 mL), and LiO(*t*-Bu) solution (from 20.9 mL 1.82 M Li(*t*-Bu) and *t*-BuOH (3.6 mL, 38.1 mol)), as for **1a** [ethanol (6 mL 95%), water (2 mL), and NaOH pellets (0.9 g, 22.5 mg-atoms), 30% hydrogen peroxide (4.2 mL), saturated brine (50 mL)], distillation at 0.9 Torr gave 1.62 g (88%) of **1e** (bp 97–9 °C). Anal. Calcd for $C_{11}H_{22}GeO$: C, 54.39; H, 9.13. Found: C, 54.47; H, 9.18. ^{13}C NMR ($CDCl_3$): δ 7.9 ($GeCH_2CH_2C$=O), 16.0 (CH_2Et), 17.7 ($CH_2CH_2CH_3$), 18.6 ($CH_2CH_2CH_3$), 38.7 (b, CH_2CH_2C=O), 214.7 (C=O) ppm. ^{1}H NMR δ 0.84 (m, 4 H), 0.93 (t, 6 H, J = 7.2 Hz), 1.05 (ct, 4 H), 1.43 (m, 4 H), 2.51 (ct, 4 H) ppm. IR (TF): 1706 cm^{-1}. MS: m/z 244 (M + (Ge - 74), 201 (M - Pr, 35), 159 (201 - C_3H_6, 100).

Acknowledgment. We are indebeted to the NIH-RCMI Program (RR03641) for the funds to purchase the GE 300-MHz NMR spectrometers (QE-300 and GN-300), which made this study possible. The support of the NSF-EPSCoR and NIH-MBRS Programs (RR08102) is gratefully acknowledged.

Registry No. **1a**, 18276-42-1; **1c**, 119996-87-1; **1d**, 41992-17-0; **1e**, 119996-88-2; **3a**, 89555-71-5; **3c**, 119996-84-8; **3d**, 119996-85-9; **3e**, 119996-86-0; **4**, 38050-71-4; divinyldimethylsilane, 10519-87-6; divinyldiethylsilane, 18270-16-1; divinyldiethylgermane, 22773-67-7; divinyldipropylgermane, 119996-89-3.

A Route to Sterically Crowded Benzophenone *N*-Aryl Imines

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While the direct condensation of an aromatic aldehyde with an aniline produces a Schiff's base with high efficiency,[1] the success of an analogous reaction with a diaryl ketone is strongly dependent on steric hindrance in both the carbonyl and amine reactants. For example, attempted reactions of benzophenone with 2,6-dimethylaniline,[2a]

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(2) (a) This work. (b) Strekowski, L.; Cegla, M. T.; Harden, D. B.; Mokrosz, J. L.; Mokrosz, M. J. *Tetrahedron Lett.* **1988**, *29*, 4265. (c) Knorr, R. *Chem. Ber.* **1980**, *113*, 2441. (d) Okubo, M.; Ueda, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 281. (e) Okubo, M.; Ueda, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3346.

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