with magnetic stirrer and bubbler and heated to reflux while Ar gas was passed through the solution for 30 min via a gas dispersion tube. The tube was removed, 540 mg of **3c** was added in one portion to the refluxing solution, and the resultant mixture (now light green) was allowed to reflux for 2 h, after which TLC analysis on silica (EtOAc–hexanes, 1:1) indicated complete reaction. The reaction mixture was cooled to +5 °C (ice bath) and acidified with methanolic HCl to pH 1. The solvent was removed under vacuum, and the residue was dissolved in 25 mL of water, extracted into $CHCl_3$ (3 × 100 mL), and dried over Na_2SO_4. The solvent was removed under vacuum to give an oil, to which 25 mL of hexanes were added, and the solution was kept in a refrigerator (+10 °C) overnight. The resultant crystals were filtered to give 490 mg (95%) of **3a**: mp 173–175 °C; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6 Hz, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 6.13 (s, 1 H, Ar), 6.25 (s, 1 H, Ar), 7.12 (s, 1 H, vinyl); IR (KBr) 3400 (br, OH), 1679 (C=O) cm^{-1}; MS m/e 344 (M^+). Anal. Calcd for $C_{21}H_{28}O_4 \cdot 0.3H_2O$: C, 72.08; H, 8.25. Found: C, 72.07; H, 8.18; H_2O (Karl Fischer), 1.42%. This material was identical spectroscopially with material prepared by Pitt et al.[5b,15] The melting point for this compound is different each time it is prepared.[16a] This may be explained by differing degrees of hydration.[16b]

Acknowledgment. We thank the Physical Chemistry staff for the spectral determinations and the Microchemistry staff for performing elemental analyses. We thank David Parrish for his intuitive input and helpful discussions concerning the homologation sequence. We also thank Laura Crowe for preparation of the manuscript.

(15) We thank Dr. C. G. Pitt of the Research Triangle Institute for graciously supplying reference NMR spectra for comparison.
(16) (a) Dr. C. G. Pitt, personal communications. (b) On a previous occasion, the monohydrate was prepared, mp 138–140 °C.

Synthesis and Properties of Cyclopropanone Hydrazones

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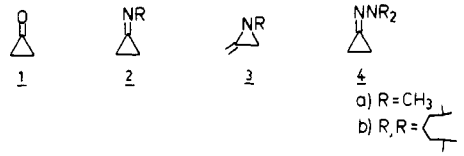
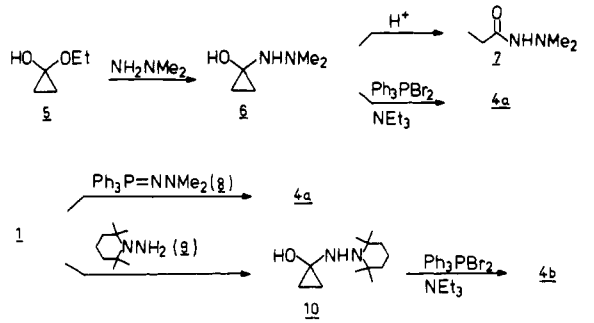
The chemistry of cyclopropanone **1** and its derivatives has been studied thoroughly.[1] Whereas **1** is extremely reactive and can only be handled in solution at low tempertures, the parent imines **2** are less sensitive.[2] Solutions



of the latter are best generated by thermal rearrangement (150–190 °C) of methyleneaziridines **3**, conditions under which partial cheletropic fragmentation to ethylene and isonitriles sets in.[2] Here we describe the synthesis, isolation, and reactivity of the novel hydrazones **4**.[3]

Upon reacting the hemiacetal **5** with *N,N*-dimethylhydrazine, the distillable but sensitive hemiaminal **6** was formed (64% yield). Unfortunately, it fails to undergo acid-catalyzed dehydration to **4a**, the hydrazide **7** being the main product. The desired transformation was finally accomplished by treatment with Ph_3PBr_2 in the presence of 2 equiv of triethylamine in dichloromethane (conversion ~40%). Alternatively, the reaction of cyclopropanone



1 with the phosphorus reagent **8**[4] also afforded **4a**. The crude product mixture was distilled rapidly to provide CH_2Cl_2 solutions of **4a** (~30% yield according to ^1H NMR spectroscopy). Pure **4a** was obtained by preparative gas chromatography. The bulky analogue **4b** is accessible by adding the hydrazine **9** to cyclopropanone and dehydrating the product **10** either by heating at 70 °C or preferably by treatment with Ph_3PBr_2/NEt_3 (64% yield).

Compound **4a** is a colorless, volatile material which is stable at −78 °C; at +4 °C decomposition sets in within 1 day. In solution at room temperature it is stable for longer periods of time. **4b** is even more stable, the pure form showing no signs of decomposition after several weeks in the refrigerator; the same applies to toluene solutions at 110 °C (4 h). Rearrangement to methyleneaziridine of the type **3** (R = amino) is not observed. All spectral and analytical data are in accord with the proposed structures. For example, the IR absorption of the C=N functionality in **4a** occurs at 1715 cm^{-1}, compared to 1680 and 1647 cm^{-1} for the *N,N*-dimethylhydrazones of cyclobutanone and cyclopentanone, respectively.[3] This is qualitatively the same trend that is observed in the ketone series itself.[1] The corresponding absorption of **4b** is shifted to 1765 cm^{-1}, probably due to steric reasons. The ^1H NMR ($DCCl_3$) spectrum shows a singlet at 2.85 ppm for the methyl groups and an AA′BB′-system for the ring protons (which was computer simulated). The ^{13}C NMR spectrum ($DCCl_3$) contains a singlet at 138 ppm (C=N) and two triplets for the other two ring C-atoms at 1.1 (J = 162 Hz) and 7.5 ppm (J = 165 Hz).

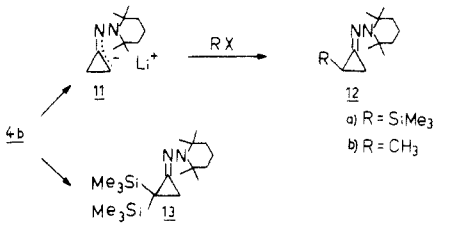
4a,b are surprisingly stable toward H_2O and CH_3OH. For example, treating a chloroform solution of **4a** with H_2O for 24 h results in only 40% loss of the compounds, i.e., more than half of it survives such conditions.

It was of synthetic interest to see if the cyclopropanone hydrazones can be alkylated via the deprotonated form without undergoing undesired polymerization. Indeed, compound **4b** can be converted into the anion **11** by treatment either with LDA (−78 °C/0.5 h) in THF or with *tert*-butyllithium (−78 °C/2 h) in ether followed by THF addition (to bring the precipitated **11** into solution). In the former case it is not certain whether deprotonation is complete or whether there is an equilibrium involving **4b**, LDA, **11**, and diisopropylamine. In any case, addition of Me_3SiCl or MeI afforded the derivatives **12a** (89%) and **12b** (56%), respectively, as distillable syn/anti mixtures.

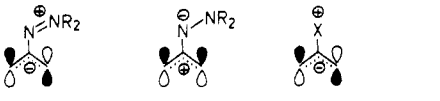
(1) Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25. Wasserman, H. H.; Clark, G. M.; Turley, P. C. *Top. Curr. Chem.* **1974**, *47*, 73. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819. Salaun, J. *Chem. Rev.* **1983**, *83*, 619. For a synthesis of the tosylhydrazone of 2,3-di-*tert*-butylcyclopropanone, see: Greene, F. D.; Camp, R. L.; Abegg, V. P.; Pierson, G. O *Tetrahedron Lett.* **1973**, 4091.
(2) Quast, H.; Risler, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 414. Quast, H.; Frank, R.; Heublein, A.; Schmitt, E. *Liebigs Ann. Chem.* **1980**, 1814. See also: Jongejan, E.; Steinberg, H.; de Boer, T. J. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 65.
(3) Rheinheimer, J. Dissertation, Universität Marburg, 1985.
(4) Zimmer, H.; Singh, G. *J. Org. Chem.* **1964**, *29*, 1579.

0022-3263/86/1951-5465$01.50/0

Upon reacting **4b** with 2 equiv of LDA and adding 2 equiv of Me_3SiCl, the bissilylated compounds **13** was obtained (77%) as a single isomer (probably anti).



Exploratory MNDO calculations[5] of the ring-opened form of **4a** with assumed planar geometry and 120° angles at sp^2 hybridized C and N atoms shows this hypothetical intermediate to have an unsymmetrical HOMO **14**, which means that this may be a more correct discription than the alternative **15**.[3] This suggests that **4a,b**, unlike cyclopropanone itself,[1] could be a precursor for $[\pi 4_s + \pi 2_s]$ cycloadditions with olefins.[6] The related hypothetical intermediate **16** (X = PMe_3) has the HOMO localized on phosphorus, but the second highest occupied MO is unsymmetrical in the allyl framework. This underlines the similarity with **14**. The nitrogen and sulfur analogues **16** also have an unsymmetrical HOMO in the allyl part. None of the species represent energy minima.



Preliminary thermolyses using **4a,b** in the presence of olefins and dienes show that electrocyclic ring opening is a high-energy process which cannot be realized in a synthetically meaningful way.[3] Derivatives of **4** having electron-withdrawing substituents at C_2/C_3 may be expected to undergo ring opening under milder conditions.

Experimental Section

IR spectra were recorded on Perkin-Elmer 457 and 577 instruments. ^1H NMR spectra were obtained on a Bruker WH 90 (90 MHz) or Bruker WH-400 (400 MHz) instrument (Me_4Si internal standard) and ^{13}C NMR spectra on a Varian XL-100 (25 MHz) or Bruker WH-400 (100 MHz) instrument. MS spectra were obtained on Varian-MAT CH7-A or Varian MAT 711 instruments. Melting points are uncorrected. Microanalyses were performed in the Analytical Section of the Fachbereich Chemie Marburg.

1-(*N,N*-Dimethylhydrazino)cyclopropanol (6). The mixture of 10.2 g (100 mmol) of 1-ethoxycyclopropanol[7] and 12.0 g (200 mmol) of *N,N*-dimethylhydrazine was heated for 2.5 h at 70 °C. The volatile components were removed at 20 °C in a rotary evaporator, and the liquid was rapidly distilled (20 min) by using an apparatus having a 15-cm Vigreux column and a Liebig cooler (−10 °C). The bath temperature should not be higher than 70 °C; the receiving bulbs were cooled to −78 °C. At 33 °C (0.1 torr), 7.4 g (64%) of **6** as a viscous colorless liquid was obtained which should be used in further reactions as soon as possible. It is stable at −35 °C for some time but decomposes at room temperature within several days. The product is >90% pure, but may contain some starting material (1-ethoxycyclopropanol), which may be the reason for the % nitrogen in the microanalysis to be too low: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.82–0.90 (m, 4 H), 2.52 (s, 6 H), 3.70 (br, 2 H); ^{13}C NMR ($CDCl_3$; 20 MHz) δ 14.8, 49.8, 68.8. Anal. Calcd for $C_5H_{12}N_2O$: C, 51.70; H, 10.41; N, 24.12. Found: C, 51.99; H, 10.49; N, 22.38.

***N,N*-Dimethyl-*N'*-(triphenylphosphoryanylidene)-hydrazine (8).** The following procedure allows the isolation and characterization of this reagent, previously obtained in solution via a related route.[4] The solution of triphenylphosphine (6.55 g; 25 mmol) in 100 mL of benzene was treated at 5 °C with 4.0 g (25 mmol) of bromine and stirred for 10 min. The solution was cooled down to −5 to −10 °C (benzene should not solidify), and a mixture of 4.6 g (25 mmol) of sodium bis(trimethylsilyl)amide and 1.5 g (25 mmol) of *N,N*-dimethylhydrazine in 30 mL of benzene and 10 mL of ether was added within 20 min. After the mixture was stirred for 30 min, an additional 4.6 g (25 mmol) of sodium bis(trimethyl)amide in benzene/ether was added, whereupon the mixture turned brown. The stirred mixture was allowed to reach room temperature overnight, the NaBr was removed by filtration, and the volatile components were removed in vacuo. The yield of crude **8** is quantitative, and the material can be used as such for further reactions. It can be recrystallized by dissolving in warm benzene (40 mL) to which 80 mL of ether was added; crystallization sets in overnight at −35 °C to provide 2.3 g (29%) of **8** as light yellow crystals, having a mp of 158 °C: IR (KBr) 3040, 2980, 2930, 2830, 2790, 2750, 1480, 1460, 1435, 1410, 1320, 1110, 1050, 1000, 940, 750, 750, 690, 540, 480, 340 cm^{-1}; ^1H NMR ($CDCl_3$ 90 MHz) δ 2.35 (s, 6 H), 7.30–7.82 (m, 15 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 51.9 (qdq, J_{P-C} = 12.9 Hz), 128.2 (dd, J_{C-H} = 162.4 Hz, J_{P-C} = 11.2 Hz), 130.8 (d, J_{P-C} = 90.6 Hz), 131.4 (dd, J_{C-H} = 161.2 Hz, J_{P-C} = 2.7 Hz), 133.2 (dd, J_{C-H} = 162.3 Hz, J_{P-C} = 8.1); MS (70 eV), *m/e* (relative intensity) 320 (17, M^+), 277 (11), 163 (22), 262 (82), 261 (11), 183 (56), 108 (28), 107 (11), 78 (100), 77 (21), 52 (18), 51 (23), 50 (17). Anal. Calcd for $C_{20}H_{21}N_2P$: C, 74.98; H, 6.61; N, 8.74. Found: C, 75.05; H, 6.68; N, 8.59.

Cyclopropanone (1). The following modification of the original procedure of Turro[9] was used. KOH (23.0 g, 500 mmol) was dissolved in H_2O to make 50 mL of a solution which was cooled to 0 °C, and 70 mL of CH_2Cl_2 was added. It was treated portionwise with 10.3 g (100 mmol) of *N*-methyl-*N*-nitrosourea. The mixture was cooled to −78 °C, and the diazomethane containing liquid part was decanted from the solidified H_2O and stored for 2 h over 15 g of solid KOH at −30 °C. About 10 mL of ketene was condensed under N_2 in a separate flask equipped with a serum cap. To the rapidly stirred ketene was added at −130 °C the cooled (−78 °C) solution of diazomethane with the aid of a syringe. The needle of a second syringe was poked through the serum cap in order to let the N_2 escape. The mixture should not be so cold that CH_2Cl_2 solidifies. After the addition was complete, the mixture was warmed to −78 °C, and the excess ketene was removed in vacuo (0.1 torr; 30–45 min) while stirring was continued. At the end of the procedure about 52 mL of a clear 1.5 M solution of cyclopropanone remained, which can be diluted with CH_2Cl_2 if so desired.

1-[(2,2,6,6-Tetramethyl-1-piperidinyl)amino]cyclopropanol (10). To a stirred solution of **1** (52.0 mL of a 1.0 M CH_2Cl_2 solution) was added at −78 °C 8.0 g (51 mmol) of 1-amino-2,2,6,6-tetramethylpiperidine. After 30 min the yield of the crude product **10** was essentially quantitative. Since attempts to isolate large amounts resulted in decomposition, the material should be used as it is in further reactions. The solvent of a small portion was evaporated in vacuo and the colorless oil analyzed: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.60–1.00 (m, 4 H), 1.09 (br s, 12 H), 1.54 (s, 6 H), 3.55 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 15.5 (t), 17.5 (t), 20.3 (br), 33.7 (br), 40.7 (t), 57.6 (s), 70.0 (s); MS (70 eV), *m/e* (relative intensity) 212 (2, M^+), 197 (2), 194 (17), 179 (18), 151 (21), 125 (27), 97 (18), 84 (11), 83 (36), 70 (29), 69 (100), 58 (66), 56 (33), 55 (82), 42 (25), 41 (74), 39 (18). Anal. Calcd for $C_{12}H_{24}N_2O$: C, 67.88; H, 11.39; N, 13.19. Found: C, 67.09; H, 11.14; N, 12.44.

***N*-Cyclopropylidene-*N',N'*-dimethylhydrazine (4a).** A stirred solution of the phosphorus reagent **8** (3.2 g; 10 mmol) in 30 mL CH_2Cl_2 was treated dropwise (30 min) with a cooled (−78 °C) solution of 29 mmol of cyclopropanone in CH_2Cl_2 (e.g., 29

(5) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(6) For reviews of cyclopentane annulation, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Paquette, L. *Top. Curr. Chem.* **1984**, *119*, 1.
(7) Salaun, J. *J. Org. Chem.* **1976**, *41*, 1237.
(8) Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540.
(9) Turro, N. J.; Hammond, W. B. *Tetrahedron* **1968**, *24*, 6017.

mL of a 1.0 M solution) at -30 to -35 °C. After addition was complete the solution was stirred for an additional hour at -35 °C. Crude distillation (0 to -10 °C bath temperature) at 0.1 torr into a cooled receiver led to essentially pure CH_2Cl_2 solutions of **4a** (polymers and phosphorus compounds remain behind). According to ^1H NMR spectral analysis the yield amounted to ca. 30%. In order to isolate a sample of **4a**, in analytically pure form, the CH_2Cl_2 was removed in vacuo until about 3-4 mL of a colorless solution remained. A portion was isolated by using GC (SE 30 column at 60 °C; receiver cooled to -78 °C): IR ($CDCl_3$) 3000, 2960, 2860, 2830, 2780, 1715, 1470, 1250, 1220, 1150, 1100; UV (*n*-hexane, qualitative) λ_{max} 225, 252 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.20-1.73 (m, AA'BB' system with δ_A at 1.32 and δ_B at 1.62, J_{gem} = -9.2 Hz, J_{trans} = 5.9 Hz, J_{cis} = 10.3 Hz, 4 H), 2.85 (s, 6 H); ^{13}C NMR ($CDCl_3$ at -10 °C, 25 MHz) δ 1.1, 7.5, 44.9 (br), 138.7; mass calcd for $C_5H_{10}N_2$ 98.0844, found (MS) 98.0845.

Alternatively, **4a** can be synthesized by dehydration of **6**. Triphenylphosphine (11.0 g; 40 mmol) in 100 mL of CH_2Cl_2 was treated with 6.4 g (40 mmol) bromine at 0 °C. To the resulting stirred white suspension was added 81 g (80 mmol) triethylamine. The mixture was cooled to -40 °C, and **6** (3.9 g; 34 mmol) in 3 mL of pentane was added dropwise. The brown mixture was stirred for 2 h at -30 °C and filtered, and the major part of the solvent was removed in vacuo at a temperature below -10 °C. The crude product contained 30-40% of **4a** (volatile **4a** was partially lost during solvent removal). The concentrated solution can be used as it is in further reactions, or solvents and product can be rapidly distilled.

1-(Cyclopropylideneamino)-2,2,6,6-tetramethylpiperidine (4b). The rapidly stirred solution of 16.2 g (60 mmol) of triphenylphosphine in 250 mL of CH_2Cl_2 was treated dropwise with 9.6 g (60 mmol) of bromine at 0 °C. After the suspension was stirred for 30 min, 12.2 g (120 mmol) of triethylamine was added, and the mixture was cooled to -35 °C. Then the cooled (-30 °C) solution of **10** (51 mmol in 50 mL of CH_2Cl_2) was added. The brown mixture was stirred 2 h at -35° C and stored at that temperature overnight. The solvent was removed in vacuo at about 10 °C until a paste-like material was obtained. It was triturated with 300 mL of pentane and filtered. The light brown residue was washed twice with 40 mL of pentane, the combined organic phases were concentrated in vacuo, and the residue was distilled [53 °C (0.1 torr)]. The colorless liquid (6.3 g; 64%) solidified in the refrigerator (mp 21 °C). In a somewhat less efficient procedure, **10** was heated in vacuo at ca. 70 °C (bath temperature), which also led to **4b**: IR (film) 2970, 2920, 2870, 1765, 1460, 1435, 1375, 1360, 1250, 1180, 1130, 1000, 975 cm^{-1}; UV (*n*-hexane) λ_{max} 216 (ϵ 1700), 332 (90) nm; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.03 (s, 12 H), 1.41-1.61 (m, 10 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 4.0 (t), 6.8 (t), 17.6 (t), 26.8 (q), 40.0 (t), 57.0 (s), 165.0 (s); MS (70 eV), *m/e* (relative intensity) 194 (27, M^+), 179 (21), 151 (18), 140 (12), 125 (27), 97 (14), 83 (31), 70 (24), 69 (100), 58 (55), 56 (27), 55 (71), 44 (18), 43 (20), 42 (69). Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.06; H, 11.67; N, 14.37.

1-[(2-(Trimethylsilyl)cyclopropylidene)amino]-2,2,6,6-tetramethylpiperidine (12a). To a stirred solution of lithium diisopropylamide (prepared at 0 °C from 330 mg (3.3 mmol) diisopropylamine in 25 mL dry THF and 1.9 mL of a 1.6 M solution of *n*-butyllithium) was added 585 mg (3.0 mmol) of **4b** at -78 °C under an atmosphere of N_2. After the mixture was stirred for 30 min at -78 °C, 350 mg (3.2 mmol) of chlorotrimethylsilane were slowly added. The stirred colorless solution was allowed to come to room temperature overnight, the solvent was removed in vacuo, 40 mL of pentane was added, and the solution was filtered. The solvent was stripped off in vacuo (0.5 torr), leaving a colorless oil **12a** (710 mg; 89%) which was essentially pure. A small portion was obtained in analytically pure form by GC (SE 30 column; 140 °C). The NMR spectra show that **12a** consists of a 2:1 mixture of *E/Z* isomers (the major isomer probably *E*): IR (film) 2970, 2930, 1750, 1435, 1370, 1360, 1250, 1180, 1130, 1105, 1025, 870, 840, 520 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.10, 1.02, 1.06, 1.15-1.60; ^{13}C NMR ($CDCl_3$, 25 MHz) δ -1.8, 5.9, 9.0, 11.7, 17.6, 17.7, 26.8, 27.1, 27.2, 27.5, 40.0, 40.4, 56.8, 57.5, 165.6, 166.7; FI-MS, *m/e* (relative intensity) 266 (100, M^+), 117 (4), 73 (5). Anal. Calcd for $C_{15}H_{30}N_2Si$: C, 67.60; H, 11.35; N, 10.51. Found: C, 67.52; H, 10.65; N, 10.54.

1-[(2-Methylcyclopropylidene)amino]-2,2,6,6-tetramethylpiperidine (12b). *tert*-Butyllithium (6.3 mL of a 1.6 M solution in hexane) was mixed with 40 mL of dry ether at -78 °C under an atmosphere of N_2. To the stirred solution was added 1.94 g 10.0 mmol) of **4b**, resulting in a white precipitate. After the mixture was stirred for 2 h at -78 °C, 20 mL of dry THF was added, which resulted in an almost clear solution. Methyl iodide (1.65 g, 11.7 mmol) was added dropwise, and the solution was stirred for 1.5 h at -78 °C and then overnight during which room temperature was reached. The clear colorless mixture was concentrated in vacuo, 60 mL of pentane was added, and the solids were removed by filtration. After removal of the solvent, distillation (15-cm Vigreux column) at 50-52 °C (0.1 torr) afforded 1.16 g (56%) of **12a** as a 2.5:1 mixture of isomers: IR (film) 2980, 2930, 2860, 1765, 1460, 1375, 1360, 1250, 1180, 1130, 975 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.03 (s), 1.19 (d, J = 8.5 Hz), 1.30 (d, J = 5.9 Hz), 1.47-2.05 (m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.4 (t), 11.7 (d), 13.9 (t), 14.4 (d), 15.8 (q), 16.3 (q), 17.6 (t), 17.7 (t), 26.9 (q), 40.1 (t), 40.3 (t), 56.6 (s), 56.7 (s), 170.0 (s), 170.5 (s); MS (70 eV), *m/e* (relative intensity) 208 (10, M^+), 193 (6), 151 (25), 125 (11), 84 (18), 83 (28), 70 (15), 69 (100), 58 (34), 57 (17), 56 (25), 55 (56), 43 (10), 42 (16), 41 (45). Anal. Calcd for $C_{13}H_{24}N_2$: C, 74.94; H, 11.61; N, 13.45. Found: C, 74.82; H, 11.77; N, 13.46.

1-[(2,2-Bis(trimethylsilyl)cyclopropylidene)amino]-2,2,6,6-tetramethylpiperidine (13). Diisopropylamine (750 mg, 7.4 mmol) in 50 mL of dry THF was treated with 4.0 mL of a 1.6 M solution of *n*-butyllithium in hexane (6.4 mmol) at 0 °C. After 15 min the solution was cooled to -78 °C, and 585 mg (3.0 mmol) of **4b** was added. The mixture remained clear and colorless. Then 690 mg (6.4 mmol) of chlorotrimethylsilane was added, and the stirred solution was allowed to reach room temperature overnight. After removal of the solvent in vacuo, 50 mL of pentane was added, and the mixture was stirred and finally filtered and concentrated. Kugelrohr distillation [150 °C (0.1 torr)] afforded 780 mg (77%) of **13** as a colorless oil, which was essentially pure. **13** exists as a single isomer, probably as shown. Additional purification can be accomplished by GC (SE 30 column, 150 °C): IR (film) 2960, 2940, 2880, 1740, 1380, 1270, 1260, 1180, 1140, 1120, 1040, 870, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.1 (s, 18 H), 1.05 (s, 12 H), 1.40 (s, 2 H), 1.54 (mc, 6 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ -0.5 (q), 6.0 (s), 12.9 (t), 17.6 (t), 27.4 (q), 40.3 (t), 57.2 (s), 164.0 (s); FI-MS, *m/e* (relative intensity) 338 (100, M^+), 267 (19), 266 (60), 213 (11), 197 (12), 125 (16), 73 (22). Anal. Calcd for $C_{18}H_{38}N_2Si_2$: C, 63.83; H, 11.31; N, 8.27. Found: C, 62.45; H, 11.12; N, 8.58.

Reaction of 4a with H_2O and CH_3OH. A solution of **4a** in chloroform was shaken with H_2O for several minutes and the mixture allowed to stand for 1 day at room temperature. Inspection of the organic phase by NMR spectroscopy showed the presence of about 60% of unreacted **4a**. A similar result was obtained by treatment with CH_3OH.

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Synthesis of Halogenated Phosphonoacetate Esters[1]

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Phosphonoacetate (PAA) derivatives are of interest for a variety of reasons, including their connection with antiviral activity.[2,3] Consequently, we have investigated

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