de l'Éducation du Québec. We are grateful to Dr. M. T. Phan Viet, who recorded our high-field NMR spectra.

Registry No. 4-Methoxybenzaldehyde, 123-11-5; 4-chlorobenzaldehyde, 104-88-1; 4-nitrobenzaldehyde, 555-16-8; cinnamaldehyde, 104-55-2; benzenepropanal, 104-53-0; 3,4-dimethyl-2,6-octadienal, 5392-40-5; 3,7-dimethyl-6-octenal, 106-23-0; 4-*tert*-butylcyclohexanone, 98-53-3; 4-nitroacetophenone, 100-19-6; benzophenone, 119-61-9; 4-methoxybenzenemethanol, 105-13-5; 4-chlorobenzenemethanol, 873-76-7; 4-nitrobenzenemethanol, 619-73-8; cinnamyl alcohol, 104-54-1; benzenepropanol, 122-97-4; 3,7-dimethyl-2,6-octadien-1-ol, 624-15-7; 3,7-dimethyl-6-octen-1-ol, 106-22-9; 4-*tert*-butylcyclohexanol, 98-52-2; α-methyl-4-nitrobenzenemethanol, 6531-13-1; 1-butanol, 71-36-3; $Ph_3SnOSnPh_3$, 1262-21-1; Ph_2SnO, 2273-51-0; $Ph_3SnOCHO$, 47182-20-7.

Preparation of α-Silylcarbanions[1]

David J. Ager

Department of Chemistry, University of Toledo, Toledo, Ohio 43606

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It has already been shown that 1-(phenylthio)-1-(trimethylsilyl)alkanes (**1**) are masked aldehydes[2,3] and, after reaction with lithium naphthalenide,[4,5] gave olefins by reaction of the resultant α-silyl anion with a carbonyl compound.[6] We now report the use of the lithium naphthalenide reaction for the preparation of substituted α-silylcarbanions, which are either difficult to prepare or are not available by other routes. The anions investigated were 1,1-bis(trimethylsilyl)-1-lithioalkanes (**2**), [tris(trimethylsilyl)methyl]lithium (**3**), 1-lithio-1-(phenylthio)-1-(trimethylsilyl)alkanes (**4**), and [bis(trimethylsilyl)-(phenylthio)methyl]lithium (**5**).

The addition of bis(trimethylsilyl)(phenylthio)methane (**6**) to lithium naphthalenide in THF at −78 °C gave [bis(trimethylsilyl)methyl]lithium (**7**),[7] which in turn reacted with nonenolizable carbonyl compounds to give the vinylsilanes (**8**) in good yield (see Table I and Scheme I). With enolizable ketones, as Seebach found,[8] the anion acted as a base and no condensation products were detected.[9] This route has two advantages over the established method of deprotonation of bis(trimethylsilyl)-methane as the synthesis of **6** is cheap and straightforward—the preparation of bis(trimethylsilyl)-methane is either long or expensive—and the use of a strong base is alleviated.[10-12]

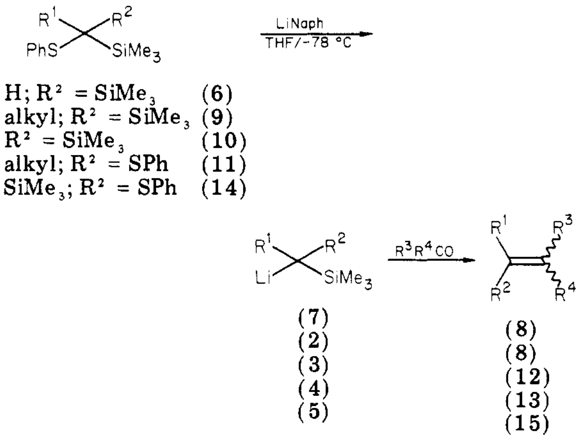
In a similar manner, the silanes **9** gave the 1-lithio-1,1-bis-(trimethylsilyl)alkanes **2**, which in turn reacted with aldehydes and nonenolizable ketones to give the vinylsilanes **8** (see Table I and Scheme I). Similar results were obtained by Seebach when the anions were formed by the addition of alkyllithiums to 1,1-bis(trimethylsilyl)ethene.[13]

In an analogous manner, tris(trimethylsilyl)(phenylthio)methane (**10**) gave [tris(trimethyl]lithium (**3**)[14] when reacted with lithium naphthalenide, while 1,1-bis(phenylthio)-1-(trimethylsilyl)alkanes **11**[15] gave 1-lithio-1-(phenylthio)-1-(trimethylsilyl)alkanes **4**. All of the anions reacted with carbonyl compounds as previously reported to give the adducts **12** or **13**, respectively, in comparable yields.[16-20]

Table I. Preparations and Reactions of α-Silylcarbanions with Carbonyl Compounds

sulfide		carbonyl compd		
R^1	R^2	R^3	R^4	product yield, %
H	$SiMe_3$ (6)	Ph	H	(8) 72 (70[8])
H	$SiMe_3$ (6)	Ph	Ph	(8) 63 (65,[8] 51[18])
H	$SiMe_3$ (6)	$-(CH_2)_5-$		(8) 0
Me	$SiMe_3$ (9)	Ph	H	(8) 69
Me	$SiMe_3$ (9)	Ph	Ph	(8) 57
Me	$SiMe_3$ (9)	H	H	(8) 71
n-Bu	$SiMe_3$ (9)	Ph	H	(8) 62
n-Bu	$SiMe_3$ (9)	Ph	Ph	(8) 48
n-Bu	$SiMe_3$ (9)	H	H	(8) 73
n-Bu	$SiMe_3$ (9)	$-(CH_2)_5-$		(8) 0
Ph	$SiMe_3$ (9)	H	H	(8) 66
$SiMe_3$	$SiMe_3$ (10)	Ph	H	(12) 68 (71[8])
$SiMe_3$	$SiMe_3$ (10)	Ph	Ph	(12) 21 (25[17])
$SiMe_3$	$SiMe_3$ (10)	H	H	(12) 73 (70[8])
$SiMe_3$	$SiMe_3$ (10)	$-(CH_2)_5-$		(12) 0
H	SPh (11)	Ph	H	(13) 70 (71,[19] 74[20])
H	SPh (11)	Ph	Ph	(13) 73 (82,[19] 78[20])
H	SPh (11)	$-(CH_2)_5-$		(13) 61 (65,[19] 68[20])
Me	SPh (11)	Ph	H	(13) 64
n-Bu	SPh (11)	Ph	H	(13) 66
n-Bu	SPh (11)	Ph	Ph	(13) 61
n-Bu	SPh (11)	H	H	(13) 71
n-Bu	SPh (11)	*n*-Bu	H	(13) 58
n-Bu	SPh (11)	$-(CH_2)_5-$		(13) 51
$SiMe_3$	SPh (14)	Ph	H	(15) 78 (76[8])
$SiMe_3$	SPh (14)	Ph	Ph	(15) 49
$SiMe_3$	SPh (14)	H	H	(15) 80 (84[8])

Scheme I



$R^1 = H; R^2 = SiMe_3$ (6)
$R^1 = alkyl; R^2 = SiMe_3$ (9)
$R^1 = R^2 = SiMe_3$ (10)
$R^1 = alkyl; R^2 = SPh$ (11)
$R^1 = SiMe_3; R^2 = SPh$ (14)

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[9] This is in contrast to anions containing one silyl group that react with carbonyl compounds as nucleophiles [see ref 6 and D. E. Seitz and A. Zapata, *Tetrahedron Lett.*, **21**, 3451 (1980)].

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[15] These compounds were prepared either by alkylation of [bis-(phenylthio)(trimethylsilyl)methyl]lithium (see Experimental Section) or by quenching the anion of the corresponding bis(phenylthio) acetal with chlorotrimethylsilane; see: D. J. Ager, *Tetrahedron Lett.*, **21**, 4763 (1980).

Finally, bis(phenylthio)bis(trimethylsilyl)methane (**14**) gave the anion **5**, which in turn gave the 1-(phenylthio)-1-(trimethylsilyl)alkanes **15** with aldehydes and nonenolizable ketones[8] (see Table I and Scheme I).

Displacement of a phenylthio group by use of lithium naphthalenide is, therefore, a useful alternative method for the synthesis of α-silylcarbanions to direct deprotonation, which besides requiring a strong base often entails a lengthy procedure for the preparation of the parent silane. The reaction, although limited in some cases to nonenolizable ketones, does yield some compounds that are useful for further elaboration.[21] The vinylsilanes and vinyl sulfides were converted to the corresponding carbonyl compounds by established procedures, and hence the anions described above are, therefore acyl anion equivalents, while the chemistry of the adducts **12** and **15** remains, to a large extent, unexplored.[21]

Experimental Section

All reactions were carried out in a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distillation from sodium-benzophenone. Lithium naphthalenide was prepared and titrated as previously described.[4,5,22]

Preparation of Bis(trimethylsilyl)(phenylthio)methane (6). (Phenylthio)(trimethylsilyl)methane[23] (3.92 g, 20 mmol), n-butyllithium (14.3 mL of a 1.4 M solution in hexane, 20 mmol), and THF (40 mL) were stirred at 0 °C for 0.5 h. Chlorotrimethylsilane (2.7 mL, 2.3 g, 21 mmol) was added and the reaction stirred for 1 h. Saturated aqueous ammonium chloride (75 mL) was added. The mixture was extracted with ether (3 × 30 mL), washed with saturated aqueous sodium chloride solution (50 mL), dried (Na_2SO_4), evaporated in vacuo, and distilled to give **6** (5.15 g, 96%): bp 137–140 °C (2 mmHg) [lit.[8] bp 88 °C (0.16 mmHg)]; IR ν_{max} (film) 1600 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.2 (5 H, m, Ph), 1.48 (1 H, s, CH), 0.08 (18 H, s, SiMe); MS, m/z 268 (57, M^+), 195 (23, M – $SiMe_3$), 110 (54, PhSH), 73 (100, $SiMe_3$).

Alkylations of 6. n-Butyllithium (7.3 mL of a 1.4 M solution in hexane, 10 mmol) was added to bis(trimethylsilyl)(phenylthio)methane (**6**; 2.68 g, 10 mmol) in THF (35 mL) at 0 °C. After 1 h the alkyl iodide (10 mmol) was added, after a further 1 h the alkyl iodide (10 mmol) was added, and after a further 1 h saturated aqueous ammonium chloride (50 mL) was added. The mixture was extracted with ether (3 × 30 mL), worked with saturated aqueous sodium chloride solution (40 mL), dried (Na_2SO_4), evaporated in vacuo, and purified by column chromatography on silica, eluting with light petroleum (bp 60–80 °C). Examples of compounds prepared by this method were as follows: **1,1-Bis(trimethylsilyl)-1-(phenylthio)ethane** (**9**, R^1 = Me, R^2 = $SiMe_3$; 2.57 g, 91%): R_f (light petroleum) 0.2; IR ν_{max} (film) 1600 (Ar C=C), 1255 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.7–7.1 (5 H, m, Ph), 1.24 (3 H, s, CMe), 0.05 (18 H, s, SiMe); MS, m/z 267 (2, M – Me), 109 (48, PhS), 73 (100, Me_3Si). Anal. Calcd for $C_{14}H_{26}SSi_2$: C, 59.5; H, 9.3. Found: C, 59.75; H, 9.1. **1,1-Bis(trimethylsilyl)-1-(phenylthio)pentane** (**9**, R^1 = n-Bu, R^2 = $SiMe_3$; 2.72 g, 84%); R_f (light petroleum) 0.2; IR ν_{max} (film) 1600 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.7–7.2 (5 H, m, Ph), 2.31 (2 H, t, J = 8 Hz, CCH_2), 1.7–1.3 (4 H, m, CH_2's), 0.87 (3 H, t, J = 8 Hz, CMe), 0.04 (18 H, s, $SiMe_3$); MS, m/z 324 (2, M^+), 309 (5, M – Me), 109 (38, PhS), 73 (100, Me_3Si). Anal. Calcd for $C_{17}H_{32}SSi_2$: C, 62.9; H, 9.9. Found: C, 63.1; H, 10.2.

Tris(trimethylsilyl)(phenylthio)methane (10). This was prepared from **6** by the method described above for alkylation but quenching the anion with chlorotrimethylsilane (1.35 mL, 1.15 g, 10 mmol) to give **10** (2.05 g, 60%) or in a one-pot reaction from (phenylthio)(trimethylsilyl)methane: n-butyllithium (7.1 mL of a 1.4 M solution in hexane, 10 mmol) was added to (phenylthio)(trimethylsilyl)methane (1.96 g, 10 mmol) in THF (20 mL) at 0 °C. After 0.5 h, chlorotrimethylsilane (1.35 mL, 1.15 g, 10 mmol) was added, followed after a further 0.5 h by n-butyllithium (7.1 mL of a 1.4 M solution in hexane, 10 mmol). Chlorotrimethylsilane (1.5 mL, 1.28 g, 11.8 mmol) was added after 1 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride (50 mL) after a further 1 h. The mixture was extracted with ether (3 × 30 mL), washed with saturated aqueous sodium chloride (50 mL), dried (Na_2SO_4), evaporated in vacuo, and purified by column chromatography on silica, eluting with light petroleum (bp 60–80 °C) to give **10** (1.77 g, 52%); R_f 0.2; IR ν_{max} (film) 1595 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.6–7.1 (5 H, m, Ph), 0.02 (27 H, s, SiMe); MS, m/z 340 (2, M^+), 251 (99, M – Me – Me_3Si), 109 (27, PhS), 73 (100, $SiMe_3$). Anal. Calcd for $C_{16}H_{32}S\ Si_3$: C, 56.4; H, 9.5. Found: C, 56.7; H, 9.65.

Alkylations of Bis(phenylthio)(trimethylsilyl)methane. n-Butyllithium (7.1 mL of a 1.4 M solution in hexane, 10 mmol) was added to bis(phenylthio)(trimethylsilyl)methane[24] (3.0 g, 10 mmol) in THF (25 mL) at 0 °C. After 1 h the alkyl iodide (10 mmol) was added and after a further 1 h saturated aqueous ammonium chloride (50 mL) was added. The mixture was extracted with ether (3 × 30 mL), washed with saturated aqueous sodium chloride (50 mL), dried (Na_2SO_4), and evaporated in vacuo to give after column chromatography (SiO_2, light petroleum) the products **11**. Examples of compounds prepared by this or the alternative method[15] were as follows: **1,1-Bis(phenylthio)-1-(trimethylsilyl)ethane** (**11**, R^1 = Me, R^2 = SPh; 2.80 g, 88%): R_f 0.2; IR V_{max} (film) 1600 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.6–7.2 (10 H, m, Ph), 1.27 (3 H, s, CMe), 0.06 (9 H, s, $SiMe_3$); MS, m/z 318 (7, M^+), 110 (63, PhSH), 73 (100, Me_3Si). Anal. Calcd for $C_{17}H_{22}S_2Si$: C, 64.0; H, 7.0. Found: C, 64,1; H, 7.3. **1,1-Bis(phenylthio)-1-(trimethylsilyl)pentane** (**11**, R^1 = n-Bu, R^2 = SPh; 2.84 g, 79%): R_f 0.2; IR ν_{max} (film) 1600 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.5–7.2 (10 H, m, Ph), 2.70 (2 H, t, J = 8 Hz, $SCCH_2$), 1.70–1.35 (4 H, m, CH_2CH_2), 0.90 (3 H, t, J = 8 Hz, CMe), –0.02 (9 H, s, SiMe); MS, m/z 260 (20, M^+), 110 (73, PhSH), 73 (100, $SiMe_3$). Anal. Calcd for $C_{20}H_{28}S_2Si$: C, 66.6; H, 7.8. Found: C, 66.5; H, 7.85.

Bis(phenylthio)bis(trimethylsilyl)methane (14). This was prepared from [bis(phenylthio)(trimethylsilyl)methyl]lithium, as described above, and chlorotrimethylsilane (1.35 mL, 1.15 g, 10 mmol) in 72% yield or from [bis(trimethylsilyl)(phenylthio)methyl]lithium, as described above, and diphenyl disulfide (2.18 g, 10 mmol) in 61% yield. Compound **14** was purified by column chromatography [SiO_2, light petroleum (bp 60–80 °C)]: R_f 0.2; IR ν_{max} (film) 1595 (Ar C=C), 1260 ($SiMe_3$) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as internal reference) δ 7.6–7.1 (10 H, m, Ph), 0.06 (18 H, s, SiMe); MS, m/z 376 (1, M^+), 361 (5, M – Me), 110 (69, PhSH), 73 (100, $SiMe_3$). Anal. Calcd for $C_{19}H_{28}S_2Si_2$: C, 60.6; H, 7.5. Found: C, 60.85; H, 7.7.

General Procedure for the Preparation of α-Silyl Anions. All of these reactions were carried out in the same manner. A typical example is as follows: 1,1-bis(trimethylsilyl)-1-(phenylthio)ethane **9**, R^1 = Me, R^2 = $SiMe_3$; 2.67 g, 10 mmol) in THF (10 mL) was added to a solution of lithium naphthalenide[22] in THF (50 mL of a 0.4 M solution, 20 mmol) at –78 °C. After 4 h at –78 °C, benzaldehyde (1.06 g, 10 mmol) in THF (10 mL) was added and the reaction allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride (100 mL) was added and the mixture extracted with ether (3 × 50 mL), washed with 2 M sodium hydroxide (2 × 50 mL) and saturated aqueous sodium chloride (50 mL), dried (Na_2SO_4), and evaporated in vacuo to give the product[25,26] **8** (R^1 = Me, R^2 = $SiMe_3$, R^3 = Ph, R^4 =

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H; 1.31 g, 69%) as approximately a 1:1.5 mixture of *Z*:*E* isomers (by NMR) after column chromatography [SiO_2, light petroleum (bp 60–80 °C)]: R_f 0.4; IR ν_{max} (film) 1595 (Ar C═C), 1260 ($SiMe_3$); NMR (CCl_4, CH_2Cl_2 as internal standard) δ 7.3 (5 H, m, Ph), 6.62 (0.5 H, q, J = 1.5 Hz, CH═C), 1.90 (3 H, dd, J = 1.5 Hz, CMe), 0.13 and 0.00 (9 H, 2 s in ratio 1.5:1, SiMe); MS, m/z 190 (36, M^+), 135 (100), 73 (89, $SiMe_3$).

Registry No. **2** (R^1 = Me), 67373-67-5; **2** (R^1 = *n*-Bu), 87739-07-9; **2** (R^1 = Ph), 87739-08-0; **3**, 28830-22-0; **4** (R^1 = H), 30536-77-7; **4** (R^1 = Me), 87729-74-6; **4** (R^1 = *n*-Bu), 87729-75-7; **5**, 62762-44-1; **6**, 62761-90-4; **7**, 41823-71-6; **8** (R^1 = H; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 18001-47-3; **8** (R^1 = H; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 51318-07-1; (*Z*)-**8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 57266-91-8; (*E*)-**8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 57266-92-9; **8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 87729-76-8; **8** (R^1 = Me; R^2 = $SiMe_3$; R^3 = R^4 = H), 18163-07-0; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 87729-77-9; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = R^4 = Ph), 71814-13-6; **8** (R^1 = *n*-Bu; R^2 = $SiMe_3$; R^3 = R^4 = H), 59549-81-4; **8** (R^1 = Ph; R^2 = $SiMe_3$; R^3 = R^4 = H), 1923-01-9; **9** (R^1 = Me), 87739-09-1; **9** (R^1 = *n*-Bu), 87729-78-0; **9** (R^1 = Ph), 87729-79-1; **10**, 87729-80-4; **11** (R^1 = H), 37891-39-7; **11** (R^1 = Me), 87729-81-5; **11** (R^1 = *n*-Bu), 87729-82-6; **12** (R^1 = R^2 = $SiMe_3$; R^3 = Ph; R^4 = H), 18415-23-1; **12** (R^1 = R^2 = $SiMe_3$; R^3 = R^4 = Ph), 78375-55-0; **12** (R^1 = R^2 = $SiMe_3$; R^3 = R^4 = H), 5654-07-9; **13** (R^1 = H; R^2 = SPh; R^3 = Ph; R^4 = H), 16619-61-7; **13** (R^1 = H; R^2 = SPh; R^3 = R^4 = Ph), 13112-46-4; **13** (R^1 = H; R^2 = SPh; R^3 = R^4 = $(CH_2)_5$), 33521-88-9; **13** (R^1 Me; R^2 = SPh; R^3 = Ph; R^4 = H), 16158-83-1; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = Ph; R^4 = H), 87729-83-7; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = Ph), 87729-84-8; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = H), 86887-88-9; **13** (R^1 = *n*-Bu; R^2 = SPh; R^3 = R^4 = $(CH_2)_5$), 87729-85-9; **14**, 87729-86-0; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = Ph; R^4 = H), 59176-57-7; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = R^4 = Ph), 87729-87-1; **15** (R^1 = $SiMe_3$; R^2 = SPh; R^3 = R^4 = H), 62762-20-3; (phenylthio)(trimethylsilyl)methane, 17873-08-4; chlorotrimethylsilane, 75-77-4; bis(phenylthio)(trimethylsilyl)methane, 37891-39-7; [bis(phenylthio)(trimethylsilyl)methyl]lithium, 87729-88-2; diphenyl disulfide, 882-33-7; [bis(trimethylsilyl)(phenylthio)methyl]lithium, 62762-44-1; benzaldehyde, 100-52-7; diphenyl ketone, 119-61-9; cyclohexanone, 108-94-1.

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Condensation of 2,3,3-Trimethyl-3*H*-indole with Methylene Iodide and Oxidative Coupling

James R. Fehlner,* Peter J. Borowski, Peter L. Pettinato, and Alan J. Freyer

Department of Chemistry, The Pennsylvania State University, The Worthington Scranton Campus, Dunmore, Pennsylvania 18512

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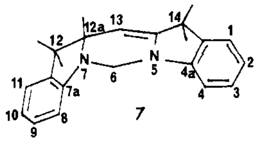
2,3,3-Trimethyl-3*H*-indole (**1**) has been coupled through the nitrogens with dihalides to give open-chain species.[1] In the case of 1,2-dihaloethane, a five-ring heterocyclic system was observed by NMR but not isolated.[2] We now describe the reaction of diiodomethane with **1** and potassium hydroxide to give the pyrimido diindole **6**, a previously unreported heterocyclic system.

The mass spectrum of **6** shows sequential loss of methyl radicals from the 12-, 12a-, and 14-positions to give an ion conjugated between the aromatic rings. Its UV spectrum is essentially identical with that of 1,3,3-trimethyl-2-methyleneindoline, confirming the presence of a similar chromophore in **6**. The indoline was also used in assigning the ^{13}C and ^1H NMR spectra of **6**.[3]

The nonequivalence of the methylene protons suggested the fused ring structure, and the proposed structure fit the ^{13}C and ^1H NMR very well. The final question was the conformation of the rings, particularly the nitrogen atoms. The nitrogens could be sp^3 or have some sp^2 character. The enamine nitrogen would be most likely to have sp^2 character. Studies of similar systems with only sp^3 nitrogens showed that cis electron pairs on the nitrogens gave large chemical shift differences between the methylenes similar to those in **6**; however, if the pairs were trans, the chemical shift differences were negligible, eliminating this possibility.

Further clarification was obtained from an evaluation of the C–H coupling constants in the ^{13}C NMR. The peaks of interest were for the 4a- (δ 144.8) and 7a- (δ 148.4) carbons. These are the aromatic carbons bonded to nitrogen. The 4a-carbon has two 8-Hz coupling constants due to coupling with the meta protons in the aromatic ring; however, the 7a-carbon has a third 8-Hz coupling, in addition to the two meta couplings, which was decoupled by irradiation of the protons at δ 4.71. It is very unlikely that the vinyl proton would have an 8-Hz coupling to either of those carbons since they would be four-bond couplings, which seldom exceed 4 Hz.[5] The third constant must therefore be due to coupling to one of the methylene protons. Lemieux's Karpus plot of $^3J_{C-N-C-H}$ vs. dihedral angle shows that an 8-Hz coupling constant would be observed for an angle of about 180°.[6] Although he has no measurements for 0° angles, one would assume that similar sized coupling constants would be observed. Of the possible conformations, (1) sp^3 nitrogens with cis electron pairs, (2) sp^2 nitrogens, and (3) an sp^2 nitrogen at position 5, with the 7-nitrogen sp^3, only in case 3 with the electron pair on the sp^3 nitrogen cis to the 12a-methyl is an 8-Hz coupling constant predicted. In this case there is an angle of about 0° between the methylene hydrogen trans to the 12a-methyl and the 7a-carbon. In cases 1 and 2 all constants are predicted to be about 1 Hz. Therefore the structure must be as shown in **7** with the hydrogen trans to the 12a-methyl absorbing at δ 4.71. The coupling of the methylene protons to the vinyl carbon at δ 151.3 is consistent with this structure. The δ 4.71 proton will be at about a 100° angle, giving neglibible coupling, while the δ 5.36 proton will be at about a 120° angle, which predicts about a 2-Hz coupling constant.



7

The size of the bridge between the nitrogens determines the type of product obtained. When the bridge is four or more carbons, coupling takes place, but no ring formation occurs.[1] A three-carbon chain does not give coupling. Instead the chain attaches to the 2-methyl on the indole ring.[7] With a two-carbon bridge an equilibrium between

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