The Preparation and Cleavage of Some 3,3-Dimethyl-3-silatetrahydrocarbazoles

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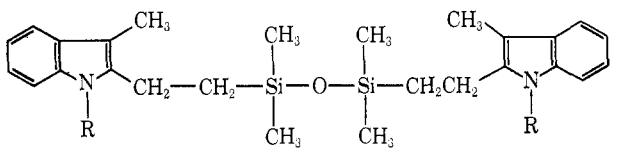
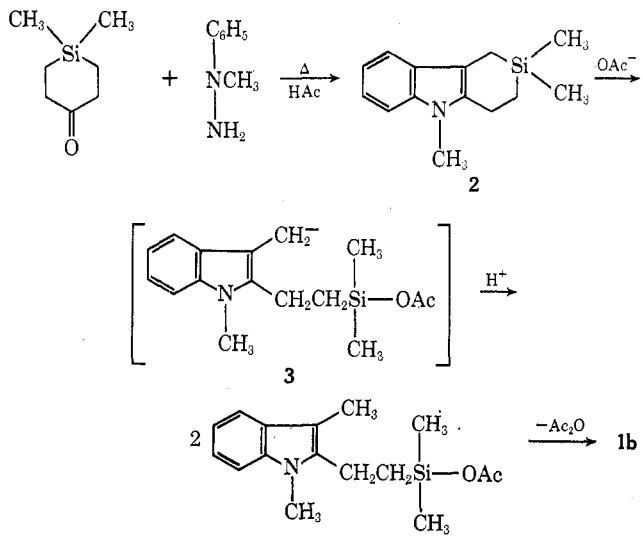
In a continuing study of polymethyleneindoles,[1] the preparation of sila analogs of tetrahydrocarbazole was undertaken. A modified Fischer indole synthesis[2] with 4,4-dimethyl-4-silacyclohexanone[3] and phenylhydrazine in refluxing glacial acetic acid (3 hr) led to an unstable, colorless product (**1a**), which underwent air oxidation to orange and then brown solids. With 1-methyl-1-phenylhydrazine, the more stable **1b** was obtained. Alkylation of **1a** with methyl iodide and dimethylaminopropyl chloride gave **1b** and **1c**, respectively. Analyses of these products established the presence of oxygen (0.5 g-atom) and led to assignment of the disiloxane structures **1a–c**; nmr spectra were consistent with the CH_2CH_2Si–O moiety.



1a, R = H
b, R = CH_3
c, R = $(CH_3)_2N(CH_2)_3$

The formation of **1** suggested that the desired dimethylsilatetrahydrocarbazole is formed early in the reaction period and is cleaved during further refluxing. When 4,4-dimethyl-4-silacyclohexanone was refluxed with 1-methyl-1-phenylhydrazine in glacial acetic acid for 5 min, a 72% yield of **2** was obtained. By refluxing **2** in acetic acid containing 15% water for 3 hr, **1b** was obtained in 65% yield. In the absence water, or when 1% water was added to the reaction mixture, no products could be isolated. The formation of **1b** from **2** is presumably initiated by nucleophilic attack of acetate ion on silicon, a reaction well known for benzylic silanes.[4] Protonation of the resonance-stabilized anion **3** and elimination of acetic anhydride then led to **1**.



Experimental Section

Melting points are uncorrected. Nmr spectra were obtained on a Varian 60-Mc spectrometer using tetramethylsilane as internal reference. The ir spectra were obtained in CCl_4, using a Perkin-Elmer Model 21 double-beam spectrophotometer. Uv spectra were obtained with a Perkin-Elmer Model 202 spectrophotometer.

Microanalysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

N-Methyl-3,3-dimethyl-3-silatetrahydrocarbazole (2).—To a solution of 2.1 g of 4,4-dimethyl-4-silacyclohexanone (0.015 mol) in 12 ml of glacial acetic acid (under nitrogen) was added, all in one portion, 2 g of 1-methyl-1-phenylhydrazine (0.015 mol + 10% excess). The mixture was refluxed exactly 5 min and allowed to cool to room temperature. The crystalline product was slurried with 20 ml of methanol and refrigerated for 3 hr. Filtering and washing twice with 5 ml of cold methanol gave crystals (3 g, 72.6%), mp 75–76°. Recrystallization from methanol gave white flakes, mp 77°.

Anal. Calcd for $C_{14}H_{19}NSi$: C, 73.30; H, 8.35; N, 6.10; Si, 12.25. Found: C, 73.42; H, 8.41; N, 6.06; Si, 12.18.

Nmr ($CDCl_3$) δ 7.45 (m, 1 H, Ar), 7.15 (m, 3 H, Ar), 3.53 (s, 3 H, N-CH_3), 2.95 (t, 2 H, J = 7 cps, CH_2-CH_2-Si), 1.85 (s, 2 H, $CH_2Si<$), 0.95 (t, 2 H, J = 7 cps, $CH_2CH_2Si<$), 0.17 [s, 6 H, $Si(CH_3)_2$]; uv max (95% EtOH) 232 mμ (ε 22,200); ir 8 μ [$Si(CH_3)_2$].

1,3-Bis[2-(1,3-dimethylindol-2-yl)ethyl]-1,1,3,3-tetramethyldisiloxane (1b).—A solution of 5.68 g of 4,4-dimethyl-4-silacyclohexanone (0.04 mol) dissolved in 30 ml of glacial acetic acid was protected by a stream of nitrogen and treated dropwise with 5.3 g of 1-methyl-1-phenylhydrazine (0.02 mol + 10%). The mixture was refluxed for 3 hr and allowed to cool until crystallization started (30 min). It was then diluted with 30 ml of acetic acid and allowed to stand for 24 hr. Filtering and washing with acetic acid gave crystals (6 g), mp 106–108°. An additional 1.6 g (mp 106–107°) was obtained from the filtrate by dilution with an equal volume of water, making a total yield of 80%. Recrystallization once from methanol gave beige crystals, mp 109–110°.

Anal. Calcd for $C_{28}H_{40}N_2OSi_2$: C, 70.53; H, 8.45; N, 5.87; Si, 11.78; mol wt, 476. Found: C, 70.26; H, 8.19; N, 6.06; Si, 11.71; mol wt, 454 (mass spectra showed M^+ at 476).

Nmr ($CDCl_3$) δ 7.3 (m, 4 H, Ar), 3.65 (s, 3 H, NCH), 2.8 (t, 2 H, J = 8 cps, $-CH_2CH_2Si=$), 2.28 (s, 3 H, -C-CH_3), 0.82 (t, 2 H, J = 8 cps, $CH_2CH_2Si=$), 0.2 [s, 6 H, $Si(CH_3)_2$]; uv max (95% EtOH) 230 mμ (ε 65,500); ir (CCl_4) 8 μ [$Si(CH_3)_2$], 9.5 (Si-O-Si).

1,1,3,3-Tetramethyl-1,3-bis[2-(3-methylindol-2-yl)ethyl]disiloxane (1a).—In a 200-ml flask equipped with a dropping funnel, nitrogen intake, and reflux condenser was placed 5.68 g of 4,4-dimethyl-4-silacyclohexanone (0.04 mol) and 30 ml of glacial acetic acid. After the mixture started to reflux, 4.8 g of phenylhydrazine (0.04 mol + 10%) was introduced dropwise. The mixture was boiled for 3 hr, allowed to cool to 60°, and 5 ml of water was added slowly, followed by 50 ml of 70% acetic acid. Refrigeration and filtration yielded a product which was recrystallized from 150 ml of methanol, weighed 4.6 g (51.3%), and melted at 117–119°. One additional recrystallization from methanol gave a product with mp 119–120°.

Anal. Calcd for $C_{26}H_{36}N_2OSi_2$: C, 69.59; H, 8.09; N, 6.24; Si, 12.52. Found: C, 69.65; H, 8.23; N, 6.09; Si, 12.77.

Nmr (CDCl) δ 7.1 (m, 5 H, Ar, NH), 2.6 (t, 2 H, J = 8 cps, CH_2CH_2Si), 2.05 (s, 3 H, $=CCH_3$), 0.75 (t, 2 H, J = cps, CH_2CH_2Si), 0.1 [s, 6 H, $Si(CH_3)_2$]; uv max (95% EtOH) 228 mμ (ε 66,500); ir (CCl_4) 8 μ [$Si(CH_3)_2$], 9.5 (Si-O-Si).

(1) (a) L. M. Rice, E. Hertz, and M. E. Freed, *J. Med. Chem.*, **7**, 313 (1964); (b) M. E. Freed, E. Hertz, and L. M. Rice, *ibid.*, **7**, 628 (1964).
(2) C. U. Rogers and B. B. Corson, *J. Amer. Chem. Soc.*, **69**, 2910 (1947).
(3) R. A. Benkeser and E. W. Bennett, *ibid.*, **80**, 5414 (1958).
(4) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, p 143.

1,3-Bis[2-(1-[3-dimethylaminopropyl]-3-methylindol-2-yl)-ethyl]-1,1,3,3-tetramethyldisiloxane (1c).—A freshly prepared solution of 15.07 g of IVa (0.07 mol) in 100 ml of dimethylformamide was stirred under nitrogen and treated with 3.7 g of sodium hydride in mineral oil (51.5%). Stirring was continued for 1 hr. γ-Dimethylaminopropyl chloride (8.9 g) was added dropwise, and the suspension was heated at 60° and stirred for 24 hr. The reaction mixture was poured into 2 l. of water and extracted with ether. The ethereal solution was extracted with 5% hydrochloric acid and the acid extract was made basic, extracted again with ether, and dried over sodium sulfate. The ether was removed and the residue was distilled giving 13.2 g of the product, bp 240–250° (0.04 mm).

Anal. Calcd for $C_{36}H_{68}ON_4Si_2$: C, 69.85; H, 9.44; N, 9.05; Si, 9.07; mol wt, 619. Found: C, 69.96; H, 9.40; N, 9.32; Si, 9.35; mol wt, 582.

The dihydrochloride was prepared with alcoholic hydrogen chloride in acetonitrile; ether was added until the solution clouded. Drying *in vacuo* at 110° gave a product that melted at 170–171°.

Anal. Calcd for $C_{36}H_{60}OCl_2N_4Si_2$: C, 62.48; H, 8.74; Cl, 10.25; N, 8.10; Si, 8.12. Found: C, 62.24; H, 8.95; Cl, 9.91; N, 8.18; Si, 7.82.

The dimethiodide, prepared in refluxing ethanol (MeOH–EtAc), had mp 145–147°.

Anal. Calcd for $C_{38}H_{64}ON_4I_2Si_2$: C, 50.55; H, 7.11; I, 28.11. Found: C, 50.43; H, 7.11; I, 27.97.

Conversion of 2 to 1b.—N-Methyl-3,3-dimethyl-3-silatetrahydrocarbazole (2) (0.5 g, 0.00218 mol) was refluxed with 6 ml of glacial acetic acid and 1 ml of water for 3 hr. When cooled to room temperature and starting to crystallize, the mixture was diluted with 2 ml of methanol and refrigerated. Later it was filtered, washed with 5 ml of methanol containing 1 ml of water, and dried giving 0.34 g (65%) of **1b**, mp 108°. One recrystallization from methanol gave material having mp 109–110°. A mixture melting point with a sample described above showed no depression, and the two materials had identical spectra.

When the same experiment was performed employing glacial acetic acid or glacial acetic acid containing only 1% water, the resulting products appeared to be mixtures, since they were of indefinite melting point (125–135°) and more highly colored.

Registry No.—**1a**, 24571-87-7; **1b**, 24571-88-8; **1c**, 24571-89-9; **1c**·2HCl, 24571-90-2; **1c**·2MeI, 24571-51-5; **2**, 24571-52-6.

Reactions of Acenaphthenequinone and Ammonium Acetate in the Presence of Aryl Aldehydes

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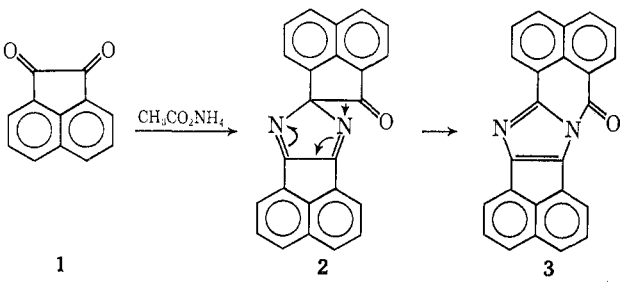
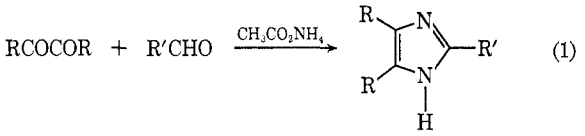
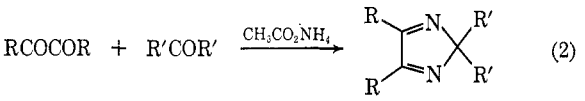
1,2 diketones and ammonium acetate in acetic acid react with arylaldehydes to form 2,4,5-trisubstituted imidazoles[1] (reaction 1) and with ketones to form 2,2,4,5-tetrasubstituted 2H-isoimidazoles[2] (reaction 2). However, with acenaphthenequinone, **1**, and salicylaldehyde, under the conditions of reaction 1, the major product is a red solid to which the imidazole structure **3** has been assigned. Product **3** is not derived from the aldehyde (*i.e.*, by reaction 1), but instead is the result of a reaction in which **1** acts both as a diketone and as a



monoketone. For reasons described below, the product does not appear to be the 2H-isoimidazole **2** which would normally be the product of reaction 2 but is **3**, a rearrangement product of **2**.



(1)



(2)

The infrared spectrum of **3** is identical with the spectrum of a compound which was isolated from the reaction of **1** with ammonia previously[3–7] and had been assigned structure **2**.[6,7] Structure **2**, however, seems less likely than **3** for several reasons. First, the ability of the reaction product to withstand temperatures as high as 400° without decomposition or rearrangement is not characteristic of isoimidazoles,[8] but is typical of imidazoles.[9] Second, the infrared spectrum of the product displays a sharp absorption band at 1500 cm^{-1} which has been found to be characteristic of arylimidazoles[10] and is also present in fused-ring imidazoles such as benzimidazole.[11] The characteristic absorption of simple 2H-isoimidazoles at 1550 cm^{-1} [10] is not present in the product. These spectral data are consistent with the structure containing the imidazole ring. Third, the deep red color of the product (λ_{max} in ethanol mμ 480) requires extensive conjugation which is present in structure **3** but not in **2** where the conjugation is interrupted by the sp^3 center in the 2 position of the isoimidazole ring. Objection to structure **2** on the basis of the color has been made by Schönberg and Singer.[5]

The composition of **3** is consistent with the elemental analysis and the high resolution mass spectrum (the most abundant peak is the parent ion at *m/e* 344.0943; calcd for $C_{24}H_{12}ON_2$, 344.0950). In addition to the

(1) (a) D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937); (b) for a review see K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, p 33.

(2) M. Weiss, *J. Amer. Chem. Soc.*, **74**, 5193 (1952).

(3) C. Graebe and E. Gfeller, *Justus Liebigs Ann. Chem.*, **276**, 1 (1893).

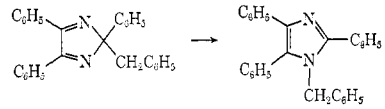
(4) A. Schönberg and F. Nedzati, *Ber.*, **54**, 238 (1921).

(5) A. Schönberg and E. Singer, *Chem. Ber.*, **98**, 3436 (1965).

(6) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jap.*, **36**, 970 (1963).

(7) O. Tsuge and M. Tashiro, *ibid.*, **39**, 2477 (1966).

(8) 2-Benzyl-2,4,5-triphenyl-2H-isoimidazole rearranges to N-benzyl-



lophine at 250° in the melt and at *ca.* 118° in acetic acid.[2] Furthermore, 2-benzoyl-2,4,5-triphenyl-2H-isoimidazole appears to rearrange to N-benzoyllophine during an intermediate step in the formation of lophine from benzil and ammonium acetate in acetic acid at *ca.* 118°.[2]

(9) See ref 1b, pp 45–46.

(10) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).

(11) K. J. Morgan, *J. Chem. Soc.*, 2343 (1961).