

The optical inversion of (+)<sub>546</sub>-Co(pyr-dtc)<sub>3</sub> in chloroform solution has been studied over a temperature range (30–50°) by following the loss of optical activity by polarimetry at 546 nm. The thermodynamic data obtained were as follows:  $E_a$ , 24.0 ± 2.1 kcal/mol;  $\Delta H^\ddagger$ , 23.4 ± 2.1 kcal/mol;  $\Delta G^\ddagger$ , 23.7 ± 4.2 kcal/mol;  $\Delta S^\ddagger$ , -0.8 ± 7.0 eu;  $A$ , 4.06 × 10<sup>12</sup> sec<sup>-1</sup>;  $k_{25^\circ}$ , 1.01 × 10<sup>-5</sup> sec<sup>-1</sup>. The near-zero entropy of activation is typical of the value previously found for a trigonal twist mechanism.<sup>3</sup>

**Acknowledgment.** Financial support from the Australian Research Grants Committee is gratefully acknowledged.

ethylenediamine leads to the stereospecific formation of the tris(ethylenediamine)cobalt(III) ion. The reaction with K[CoPDTA] described in the present paper appears not to be stereospecific since in a number of preparations the optical activity of the product is lower than that obtained using K[CoEDTA].<sup>8</sup>

(8) (a) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **80**, 4480 (1958); (b) H. Irving and R. D. Gillard, *J. Chem. Soc.*, 2249 (1961); (c) D. H. Busch, K. Swaminathan, and D. W. Cooke, *Inorg. Chem.*, **1**, 260 (1962).

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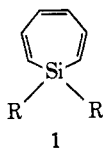
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Received November 12, 1973

## Synthesis of

### 1,1-Dimethyl-2,7-diphenyl-1-silacyclohepta-2,4,6-triene. A Nonannulated Silepin

Sir:

Despite considerable activity in the area of heterocycloheptatrienes,<sup>1</sup> there have been no substantiated<sup>2</sup> reports of nonannulated<sup>3</sup> silacycloheptatrienes, silepins (1), to date. Aside from the usual desire to study the



properties of a new ring system, interest in 1 is derived from its possible role as a precursor to the unknown<sup>11</sup>

(1) For an excellent review of the syntheses and chemistry of azepines, oxepines, and thiepins, see L. A. Paquette in "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1970, pp 249–310.

(2) A hexaphenyldicarbomethoxysilepin structure has been tentatively suggested for the product from ethanol induced decomposition of a 7-silanorbornadiene: H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 5584 (1964).

(3) Annulated silepins known are the benzo[d]silepin,<sup>4,5</sup> the dibenzo[b,f]silepin,<sup>6,7,8</sup> and the tribenzo[b,d,f]silepin.<sup>9,10</sup>

(4) L. Birkofer and H. Haddad, *Chem. Ber.*, **102**, 432 (1969); **105**, 2101 (1972).

(5) L. Birkofer, H. Haddad, and H. Zamarlik, *J. Organometal. Chem.*, **25**, C57 (1970).

(6) J. Y. Corey, M. Deuber, and B. Bichlmeir, *J. Organometal. Chem.*, **26**, 167 (1971).

(7) F. K. Cartledge and P. D. Mollere, *J. Organometal. Chem.*, **26**, 175 (1971).

(8) T. J. Barton, W. E. Volz, and J. L. Johnson, *J. Org. Chem.*, **36**, 3365 (1971).

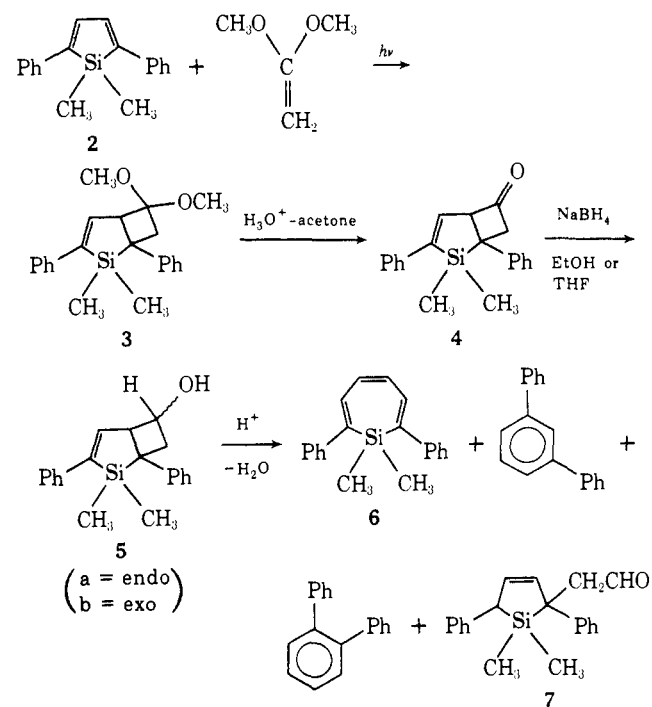
(9) K. A. Andrianov, L. M. Volkova, N. V. Delazari, and N. A. Chumaeski, *Khim. Geterotskil. Soedin.*, 435 (1967); *Chem. Abstr.*, **67**, 10869c (1967).

(10) J. Y. Corey and E. R. Corey, *Tetrahedron Lett.*, 4669 (1972).

(11) An exception to this is the frequent and abundant observation of R<sub>3</sub>Si<sup>+</sup> in the mass spectra of various organosilanes.

silylenium ion (R<sub>3</sub>Si<sup>+</sup>) and as a model system in which to search for cyclic (p-d-p)π conjugation.<sup>12</sup>

Our synthesis starts with the photoaddition of 1,1-dimethoxyethylene to the readily available<sup>13</sup> 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (2). Although plagued by the photolability of 2,<sup>14</sup> irradiation (N<sub>2</sub>, medium-pressure 450-W Hg arc through Pyrex) of 2 dissolved in 1,1-dimethoxyethylene (ca. 1 g/60 ml) affords ketal (3) in 70% yield (mp 86.5–87.5°; nmr<sup>15</sup> (DCCl<sub>3</sub>) δ 7.30–6.80 (m, 11 H), 3.70 (d, 1 H,  $J = 3.5$  Hz), 3.09 (s, 6 H), 2.74 and 2.42 (AB, 2 H,  $J = 12$  Hz), 0.41 (s, 3 H), -0.21 (s, 3 H)).<sup>16</sup> Hydrolysis of 3 was effected with slightly acidic aqueous acetone to yield ketone 4 in 72% yield (mp 72–73°; nmr<sup>15</sup> (CCl<sub>4</sub>) δ 7.28–6.90 (m, 10 H), 6.86 (d, 2 H,  $J = 4$  Hz), 4.49 (m, 1 H), 3.61 (d of d, 1 H,  $J = 11$  and 2 Hz), 3.35 (d of d, 1 H,  $J = 11$  and 1 Hz), 0.40 (s, 3 H), -0.11 (s, 3 H); ir  $\nu_{C=O}$  (neat) 1785 cm<sup>-1</sup>).<sup>16</sup> Sodium borohydride reduction of 4 provided 5 as a ca. 1:1 epimeric mixture of alcohols in 52% yield. Tedious fractional recrystallization afforded pure endo alcohol (5a) (mp 115–116°; nmr<sup>15</sup> (DCCl<sub>3</sub>) δ 6.98–7.50 (m, 10 H), 6.94 (d, 1 H), 4.49 (br s, 1 H), 3.98 (d of d of d (apparent d of t), 1 H,  $J = 2.5, 3,$  and 8.5 Hz), 2.82 (d of d of d, 1 H,  $J = 12, 2.5,$  and 7.5 Hz), 2.43 (d of d, 1 H,  $J = 7.5$  and 12 Hz), 1.82 (br s, 1 H, exchanges with D<sub>2</sub>O), 0.42 (s, 3 H), -0.17 (s, 3 H)).<sup>16</sup> The exo alcohol (5b) has not been obtained in pure form but has been completely characterized as the *p*-nitrobenzoate derivative.



The most successful method for dehydration of 5a has been with a catalytic amount of *p*-toluenesulfonic

(12) An excellent, detailed discussion of (pd)π cyclic conjugation is provided by G. Hafelinger, *Fortschr. Chem., Forsch.*, **28**, 1 (1972).

(13) T. J. Barton and E. E. Gottsman, *Syn. Inorg. Metal-Org. Chem.*, **3**, 201 (1973).

(14) T. J. Barton and A. J. Nelson, *Tetrahedron Lett.*, 5037 (1969).

(15) Extensive discussion of the nmr spectra and mechanistic speculation is deferred to the complete manuscript.

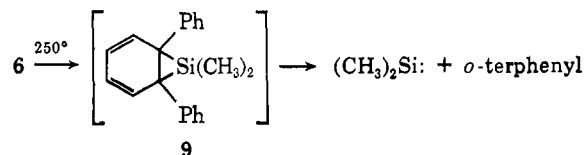
(16) All new compounds reported here with the exception of 7 gave satisfactory elemental (C and H) analysis and consistent ir, nmr, and mass spectra. Aldehyde 7 was unstable, did not give reproducible values, and was characterized solely from spectral data.

acid in benzene with azeotropic removal of water (recirculating Dean-Stark trap filled with Linde 4A molecular sieves). Chromatography of the reaction mixture on silica gel provided (hexane elution) a mixture of *m*-terphenyl (24%),<sup>15</sup> *o*-terphenyl (ca. 3%), and 1,1-dimethyl-2,7-diphenyl-1-silacyclohepta-2,4,6-triene (**6**) (ca. 11%). Further elution with 1:1 hexane-ether removed 1,1-dimethyl-*cis*-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (**7**) (colorless oil; 12.2%; nmr<sup>15</sup> (CCl<sub>4</sub>)  $\delta$  9.44 (m, 1 H), 6.80–7.40 (m, 10 H), 6.21 (d of d, 1 H,  $J = 7$  and 3 Hz), 6.00 (d of d, 1 H,  $J = 7$  and 2 Hz), 3.24 (br s, 1 H), 3.04 (d of d, 1 H,  $J = 18$  and 2 Hz), 2.51 (d of d, 1 H,  $J = 18$  and 3 Hz), 0.26 Os, 3 H),  $-0.78$  (s, 3 H); ir  $\nu_{C=O}$  (neat) 1727 cm<sup>-1</sup>; mass spectrum (70 eV)  $m/e$  304 (M<sup>+</sup>).<sup>16</sup> Aldehyde **7** was found to be quantitatively formed from **5a** in a 300° flow pyrolysis.

In our hands the silepin (**6**) could not be completely purified from the terphenyls with gc, tlc, or fractional crystallization. However liquid chromatography (4 ft  $\times$   $\frac{3}{8}$  in. Bondapak C<sub>18</sub>/Porasil B column with MeCN-H<sub>2</sub>O as carrier solvent) allowed clean separation of **6** (mp 60–61°).

The question of the geometry of **6** is a crucial one as ring planarity would imply significant cyclic (p-d-p) $\pi$  delocalization<sup>12</sup> providing a neutral analog of the tropylium cation. The methyl protons of **6** appear as one singlet ( $\delta$  0.10)<sup>17</sup> in the nmr spectrum which can be accounted for by a rapidly inverting boat geometry, a planar geometry, or a noninverting boat with fortuitous nmr equivalence.<sup>10</sup> The latter possibility may be discounted as even with no cyclic delocalization a very low barrier for inversion of boat forms would be predicted from the calculations of Allinger<sup>18</sup> for benzo- and dibenzosilepins. To distinguish between inverting boat and planar geometry, spectral comparison of **6** and a model compound of reasonably certain geometry was employed. An excellent model compound for **6** is 1,6,7-triphenyltropilidene (**8**) which was prepared from Diels-Alder addition of  $\alpha$ -pyrone to 1,2,3-triphenylcyclopropene followed by thermal extrusion of CO<sub>2</sub>. The vinyl protons of **8** appear as an AA'BB' eight-line spectrum (lower field protons exhibit slight allylic coupling) with centers at  $\delta$  6.40 and 6.71,  $J$  apparent = 3.0, 4.5 Hz. This is remarkably similar to the olefinic spectrum of **6** which is also an AA'BB' eight-line pattern with centers at  $\delta$  6.51 and 6.80,  $J$  apparent = 3.0, 4.5 Hz. This would imply that **6** possesses the same geometry as **8** which can be assumed to be *inverting boat*. The uv spectrum of **6** ( $\lambda_{max}^{MeCN}$  (log  $\epsilon$ ) 234 (4.29), 320 (4.04)) is rather similar to that of **8** ( $\lambda_{max}^{MeCN}$  (log  $\epsilon$ ) 259 (4.38), 330 (3.99)). Thus it would appear that cyclic conjugation through silicon does not control the geometry of **6**. If indeed such bonding is present, the only effect may be a possible lowering of the inversion barrier through stabilization of the planar form.

Pyrolysis of **6** (sealed tube, 250°, 15 min) cleanly afforded *o*-terphenyl. This was expected from the reported thermal conversion of benzo[*d*]silepins to naphthalene.<sup>4,5</sup> This is of considerable interest as the elimination presumably takes place through the inter-



mediacy of the silanorcardiene (**9**)<sup>19</sup> and thus would involve the until recently unknown<sup>20</sup> silacyclopropane.

**Acknowledgment.** This research was supported by Grant No. GM 16689 from the National Institutes of Health, Public Health Service. The technical assistance of Mr. Louis E. Sartori of Waters Associates, Inc. in the separation of **6** by liquid chromatography is gratefully acknowledged.

(19) Such a mechanism is most commonly used to explain conversion of thiopins to benzenes through sulfur extrusion: B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, Oxford, 1967.

(20) R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972).

(21) Gulf Oil Predoctoral Fellow, 1971–1972.

(22) NASA Predoctoral Fellow, 1969–1972.

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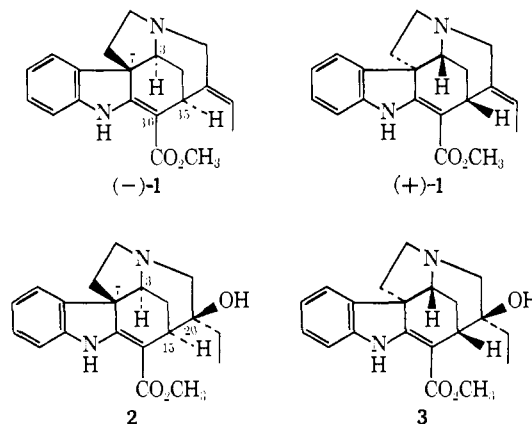
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Received August 29, 1973

### A Laboratory Model for the Biogenesis of the "Antipodal" Strychnos Alkaloids

Sir:

The discovery of enantiomeric forms<sup>1</sup> of the *Strychnos* alkaloid akuammicine (**1**) and the diastereoisomers (–)-lochneridine (**2**) and (+)-20-epilochneridine<sup>2</sup> (**3**) has



presented a long standing problem<sup>3</sup> in terms of the absolute stereochemistry of the biogenetic pathway to (+)-**1** and **3**. Thus a nonstereospecific step involving C<sub>15</sub> has been invoked<sup>1</sup> to account for the difficulty in arriving at a plausible mechanism for the inversion of stereochemistry at C<sub>3</sub>, C<sub>7</sub>, and C<sub>15</sub> in **1** and **2** which would surely involve rupture of the C<sub>3</sub>–C<sub>7</sub> and C<sub>15</sub>–C<sub>16</sub> bonds. Biosynthetic experiments<sup>4</sup> have revealed that

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(3) J. E. Saxton in "The Alkaloids," Vol. VIII, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1965, Chapter 7; Vol. X, 1968, Chapter 11.

(4) A. I. Scott, P. C. Cherry, and A. A. Qureshi, *J. Amer. Chem. Soc.*, **91**, 4932 (1969); A. R. Battersby and E. S. Hall, *Chem. Commun.*, 793 (1969).

(17) No splitting of this peak is observed with lower temperatures although broadening is seen at  $-95^\circ$  in CS<sub>2</sub>.

(18) N. L. Allinger, R. A. Greengard, and C. J. Finder, *Tetrahedron Lett.*, 3095 (1973).