

**N-(2,2-Diethoxyethyl)-1-(3-(trifluoromethyl)phenyl)-2-propylamine (21):** bp 109–111 °C (0.05 mm); IR (neat) 2980, 2900, 1600, 1450, 1320, 1200, 1150, 1060, 800, 705  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.15 (m, 9 H), 2.4–3.4 (m, 6 H), 3.4–4.2 (m, 4 H), 4.85 (t, 1 H,  $J = 6$  Hz), 7.9 (s, 4 H).

Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{F}_3\text{NO}_2$ : C, 60.17; H, 7.57; F, 17.84; N, 4.38; O, 10.01. Found: C, 60.08; H, 7.55; F, 18.01; N, 4.47; O, 9.89.

**Acknowledgment.** We would like to thank Mr. David St. Maurice and his staff for the excellent analytical services.

**Registry No.** 1a, 24743-14-4; 1h, 300-57-2; 1i, 1813-96-3; 2a, 71250-18-5; 2b, 71250-19-6; 2c, 71250-20-9; 2d, 71250-21-0; 2e, 71250-22-1; 2f, 71250-23-2; 2g, 71250-24-3; 2h, 1085-43-4; 2i, 14818-01-0; 2j, 71250-25-4; 2k, 404-82-0; 2l, 71250-26-5; 3c, 71250-27-6; 3d, 71250-28-7; 3g, 71250-29-8; 3h, 53578-37-3; 3j, 71250-30-1; 3k, 71250-31-2; 3l, 71250-32-3; aminoacetaldehyde diethyl acetal, 645-36-3; 1-butanamine, 109-73-9; benzenemethanamine, 100-46-9; diethylamine, 109-89-7; benzenamine, 62-53-3; morpholine, 110-91-8; 4-phenylpiperidine, 771-99-3; ethanamine, 75-04-7; mercury perchlorate, 7616-83-3; mercury nitrate, 10045-94-0.

### Stereochemistry of the Diels–Alder Reaction of Vinylcyclohexene or 1-[ $\alpha$ -(*tert*-Butyldimethylsilyloxy)vinyl]- $\Delta^1$ -cyclohexene and 2-Methylcyclopentenone

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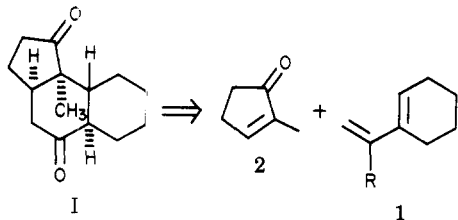
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As part of an investigation on the total synthesis of the macrolide antibiotic chlorothricolide,<sup>1</sup> an efficient synthesis of a *cis*-*anti*-*trans* fused tricyclic ring system such as I was required. A simple, convergent approach to the construction of such a tricyclic I might be the Diels–Alder reaction of a vinylcyclohexene (1) with 2-methylcyclopentenone (2).



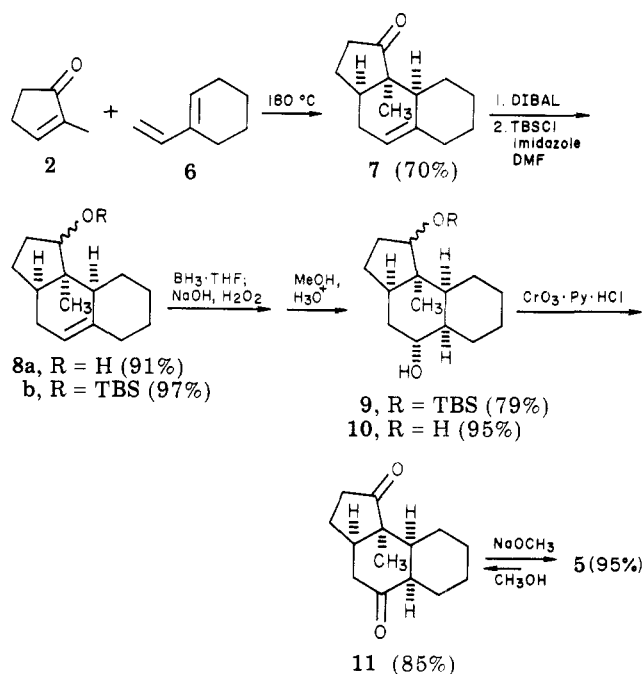
Indeed, the reaction between vinylcyclohexene (1, R = H) and 2-methylcyclopentenone (2) was reported in 1939 by Bockemuller to give an adduct of unknown structure.<sup>2</sup> While many examples of this type of Diels–Alder reaction have been reported, evidence for the stereochemical outcome of the reaction resulting from the two possible modes of cycloaddition is usually only speculative.<sup>3</sup> Of

(1) W. Keller-Schierlein, R. Muntwyler, W. Pache, and H. Zähler, *Helv. Chim. Acta*, **52**, 127 (1969); R. Muntwyler, J. Widmer, and W. Keller-Schierlein, *ibid.*, **53**, 1544 (1970); R. Muntwyler and W. Keller-Schierlein, *ibid.*, **55**, 2071 (1972); M. Brufani, S. Cerrini, W. Fedeli, F. Mazza, and R. Muntwyler, *ibid.*, **55**, 2094 (1972).

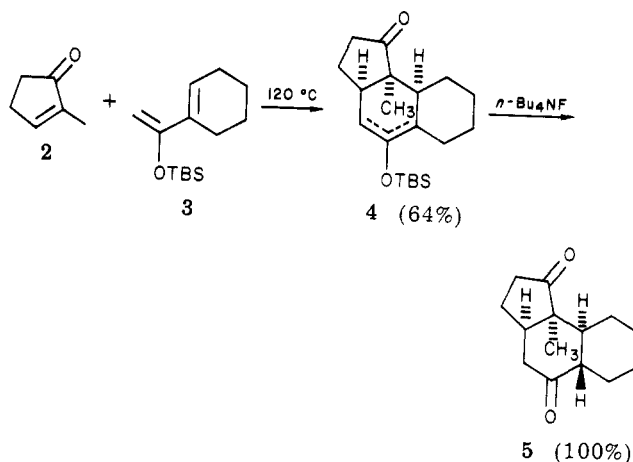
(2) W. Bockemuller, U.S. Patent 2 179 809 (1939); *Chem. Abstr.*, **34**, 1823 (1940).

(3) A. S. Onischenko, "Diene Synthesis", Israel Program for Scientific Translations, Jerusalem, 1964, pp 416–425, and references cited therein.

### Scheme I



those rare cases where a rigorous structure proof is given, *anti* or *syn* products resulting from either predominant *exo* or *endo* cycloaddition can be found.<sup>4</sup> We report here the results of a single-crystal X-ray diffraction analysis of the tricyclic dione 5 from the Diels–Alder reaction of 1-[ $\alpha$ -(*tert*-butyldimethylsilyloxy)vinyl]- $\Delta^1$ -cyclohexene (3) and 2-methylcyclopentenone (2). The diene 3 was prepared



in 79% distilled yield by enolization of acetylcyclohexene with lithium diisopropylamide (LDA) at  $-78$  °C, and then trapping the resulting dienolate anion with *tert*-butyldimethylsilyl chloride (TBSCl) in hexamethylphosphoramide (HMPA). The Diels–Alder adduct 4, which consisted of a mixture of silyl enol ether double bond isomers, was converted quantitatively to the dione 5 by treatment with tetra-*n*-butylammonium fluoride in tetrahydrofuran (THF).<sup>5</sup>

The dione 5 was found to have identical physical properties (mixture melting point,  $^1\text{H}$  NMR, IR) to a dione obtained by chemical modification of the Diels–Alder

(4) M. F. Ansell and G. T. Brooks, *J. Chem. Soc.*, 4518 (1956); I. N. Nazarov, V. F. Kucherov, and G. M. Segal, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1215 (1956); I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, *ibid.*, 331 (1957); I. N. Nazarov, V. F. Kucherov, V. M. Andreev, and G. M. Segal, *Croat. Chim. Acta*, **29**, 369 (1957); F. Winternitz and C. Balmossiere, *Tetrahedron*, **2**, 100 (1958).

(5) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

adduct from vinylcyclohexene (6) and 2-methylcyclopentenone (2) (Scheme I).

The X-ray analysis revealed that the dione 5 possessed the cis-syn-trans fused structure rather than the desired cis-anti-trans fused ring skeleton (Figure 1).

The reaction of 2-methylcyclopentenone (2) and a vinylcyclohexene such as 3 or 6 must therefore give almost exclusively the cis-syn adduct, in keeping with the general preference for endo orientation in the Diels-Alder reaction.

### Experimental Section<sup>6</sup>

**1-[ $\alpha$ -(*tert*-Butyldimethylsilyloxy)vinyl]- $\Delta^1$ -cyclohexene (3).** To a rapidly stirred solution of 19.3 mmol of lithium diisopropylamide [from 3.3 mL (23 mmol) of diisopropylamine and 19.3 mmol of *n*-butyllithium in hexane] in 38 mL of dry THF cooled to  $-78^\circ\text{C}$  with a dry ice-acetone bath was added dropwise 2.0 g (16 mmol) of acetylcyclohexene<sup>7</sup> in 16 mL of dry THF. The resulting mixture was allowed to stir at  $-78^\circ\text{C}$  for 10 min and 13.5 mL of a 1.5 M solution of *tert*-butyldimethylsilyl chloride in dry HMPA was added dropwise over  $\sim 10$  min. The mixture was allowed to warm to room temperature over 30 min, then diluted with 100 mL of pentane and washed twice with 100-mL portions of water and saturated aqueous NaCl solution. After drying over  $\text{MgSO}_4$ , removal of solvents under reduced pressure afforded a yellow oil which was evaporatively distilled at 120–140  $^\circ\text{C}$  (0.05 mmHg) to afford 3.0 g (79%) of the silyloxy diene 3: IR ( $\text{CCl}_4$ ) 1600 (m), 1270 (s), 840 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (s, 6 H,  $(\text{CH}_3)_2\text{Si}$ ), 0.96 (s, 9 H,  $(\text{CH}_3)_3\text{C}$ ), 1.57 (br m, 4 H,  $\text{CH}_2\text{CH}_2$ ), 2.1 (br m, 4 H, allylic H's), 4.13 (br s, 1 H, vinyl H), 4.27 (br s, 1 H, vinyl H), 6.17 (br m, 1 H, vinyl H).

Anal. Calcd for  $\text{C}_{14}\text{H}_{28}\text{OSi}$ : C, 70.52; H, 10.99. Found: C, 70.65; H, 11.01.

**5-(*tert*-Butyldimethylsilyloxy)-9 $\beta$  $\alpha$ -methyl-2,3,3 $\alpha$ ,4,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1*H*-cyclopenta[*a*]naphthalen-1-one and 5-(*tert*-Butyldimethylsilyloxy)-9 $\beta$  $\alpha$ -methyl-2,3,3 $\alpha$ ,5 $\alpha$ ,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1*H*-cyclopenta[*a*]naphthalene-9-one (4).** A thick-wall Pyrex tube was charged with a mixture of 1.2 g (12.4 mmol) of 2-methylcyclopentenone (2),<sup>8</sup> 1.3 g (5.5 mmol) of the diene 3, and a few crystals of hydroquinone. After degassing with two freeze-pump-thaw cycles, the tube was sealed under vacuum while the contents remained frozen. The sealed tube was heated to 180  $^\circ\text{C}$  for 12 h, cooled until the contents was frozen in a liquid nitrogen bath and opened. After removal of solvents under reduced pressure, chromatography of the crude residue on silica gel using benzene afforded 1.2 g (64%) of the ketones 4 as a mixture of double bond isomers: IR ( $\text{CCl}_4$ ) 1740 (vs), 1600 (m), 1270 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.08 (s,  $\text{CH}_3\text{Si}$ ), 0.12 (s,  $\text{CH}_3\text{Si}$ ), 0.92 (s,  $(\text{CH}_3)_3\text{C}$ ), 1.08 (s,  $\text{CH}_3$ ), 4.63 (br m, vinyl H).

Anal. Calcd for  $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}$ : C, 71.80; H, 10.24. Found: C, 71.84; H, 10.26.

**9 $\beta$  $\alpha$ -Methyl-2,3,3 $\alpha$ ,4,5,5 $\alpha$ ,6,7,8,9,9 $\alpha$ ,9 $\beta$ -dodecahydro-1*H*-cyclopenta[*a*]naphthalene-1,5-dione (5).** A solution of 1.0

(6) Melting points were taken using a Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were determined on either a Perkin-Elmer 727B or Beckman 4210 infrared spectrometer, and nuclear magnetic resonance ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR) spectra were recorded using either a Varian T-60 or EM-390 spectrometer. The Varian T-60 was modified with a Nicolet Technology Corporation TT-7 pulsed rf Fourier transform system. Thin-layer chromatography was performed on E. Merck TLC plates 60F-254, 0.25 mm. All silica gel used for column chromatography was E. Merck "Silica Gel 60", 70–230 mesh ASTM. "Dry" solvents and reagents were distilled shortly before use from an appropriate drying agent. Ether and THF were distilled under a dry argon atmosphere from sodium metal using benzophenone ketyl as an indicator. Dichloromethane was distilled from phosphorus pentoxide. Dimethylformamide (DMF) was distilled from silica gel. HMPA was distilled at 0.5 mm from pulverized calcium hydride. Diisopropylamine was distilled from calcium hydride under an argon atmosphere. All other solvents were "reagent grade" unless described otherwise. Analytical samples were obtained by evaporative distillation at 0.01 mm, unless otherwise indicated. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

(7) S. B. Kulkarni and S. Dev, *Tetrahedron*, **24**, 553 (1968).

(8) 2-Methylcyclopentenone (2) was synthesized from 1-methylcyclopentene as described by Rinkes<sup>9a</sup> using the modified procedure of Reitsma<sup>9b</sup> for the addition of nitrosyl chloride.

(9) (a) I. J. Rinkes, *Recl. Trav. Chim. Pays-Bas*, **57**, 176 (1938); (b) R. H. Reitsma, *J. Org. Chem.*, **23**, 2038 (1958).

g (3 mmol) of the silyl enol ether 4 in 12 mL of dry THF was treated with 2.3 g (8.9 mmol) of tetra-*n*-butylammonium fluoride<sup>5</sup> under an argon atmosphere for 1 h at room temperature. The mixture was diluted with ether, washed with water, and dried over  $\text{MgSO}_4$ . Removal of solvents under reduced pressure and chromatography of the crude residue over silica gel using 5% ethyl acetate in benzene afforded 0.65 g (100%) of crystalline dione 5: mp 74–76  $^\circ\text{C}$ ; IR ( $\text{CCl}_4$ ) 1740 (vs), 1720 (vs), 1460 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.18 (s, 3 H,  $\text{CH}_3$ ).

An analytical sample was prepared by recrystallization from cyclohexane: mp 75.5–76  $^\circ\text{C}$ .

Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_2$ : C, 76.33; H, 9.15. Found: C, 76.29; H, 9.10.

**Crystallographic Study of the Dione 5.** Colorless crystals of the tricyclic dione 5 were grown from cyclohexane. The space group was determined to be  $P2_1/c$ . The cell constants were found to be  $a = 7.879$ ,  $b = 18.908$ ,  $c = 8.344$   $\text{\AA}$ ,  $\beta = 105.03^\circ$ ,  $\rho_{\text{obsd}} = 1.221$   $\text{g/cm}^3$ ,  $\rho_{\text{calcd}} = 1.219$   $\text{g/cm}^3$ , and  $Z = 4$ .

The diffraction data were collected by the  $\theta$ - $2\theta$  scan technique on a Syntex P2<sub>1</sub> automated diffractometer at room temperature with  $\text{Mo K}\alpha$  radiation. The scan rate varied from 2 to 10 $^\circ$ /min dependent on the intensity of the diffraction maxima. The base width was 2 $^\circ$ , and the sum of the background counting times equalled one-half the total scan time. No decay was noted in the three check reflections monitored every 50 reflections. A total of 843 reflections was collected out to a maximum  $2\theta$  of 40 $^\circ$ ; 718 reflections had intensities greater than  $3.0\sigma(I)$ .

The structure was solved using the direct methods program MULTAN and three-dimensional Fourier calculations. Hydrogen atom positions were calculated using standard bond distances and angles. The structure was refined by block-diagonal least-squares calculations to a final  $R$  value of 0.04 and a goodness-of-fit of 2.28 on the 718 observed data by a Gauss-Seidel block-diagonal least-squares calculation. The calculated hydrogen atom positions were only included in the structure factor calculations. The scattering factors were calculated by the analytical approximation  $f_s = \sum a_i \exp(-b_i S^2)$ . Bond distances and angles are all within acceptable values. The molecules are held together by van der Waals interactions.

All calculations were carried out on the Data General Eclipse S230 computer in the diffraction laboratory using local programs and programs adapted from elsewhere which together comprise the crystallographic structure solving package CRYSP 78.

**9 $\beta$  $\alpha$ -Methyl-2,3,3 $\alpha$ ,4,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1*H*-cyclopenta[*a*]naphthalen-1-one (7).** A mixture of 3.3 g (30 mmol) of vinylcyclohexene<sup>10</sup> and 3.0 g (31 mmol) of 3-methylcyclopentenone (2)<sup>8</sup> containing a few crystals of hydroquinone was placed in a thick-wall Pyrex tube and sealed under vacuum while frozen (liquid nitrogen bath) after two freeze-pump-thaw cycles. The tube was heated to 190  $^\circ\text{C}$  for 10 h, then cooled until frozen in a liquid nitrogen bath and opened. After removal of the solvents under reduced pressure, chromatography of the crude residue on silica gel using 5% ethyl acetate in cyclohexane afforded 4.3 g (70%) of the ketone 7 as a colorless oil: IR ( $\text{CCl}_4$ ) 1740 (vs), 1480 (w), 1460 (w), 1455 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.0 (s, 3 H,  $\text{CH}_3$ ), 5.23 (br m, 1 H, vinyl H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.5, 25.5, 25.8, 28.4, 29.0, 33.2, 37.7, 41.7, 44.1, 49.5, 115.7, 138.5, 220.1.

Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}$ : C, 82.30; H, 9.87. Found: C, 82.34; H, 9.87.

**1 $\beta$ -Hydroxy-9 $\beta$  $\alpha$ -methyl-2,3,3 $\alpha$ ,4,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1*H*-cyclopenta[*a*]naphthalene and 1 $\alpha$ -Hydroxy-9 $\beta$  $\alpha$ -methyl-2,3,3 $\alpha$ ,4,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1*H*-cyclopenta[*a*]naphthalene (8a).** To a stirred solution of 1.0 g (5 mmol) of the ketone 7 in 25 mL of dry ether cooled to 0  $^\circ\text{C}$  in an ice bath was added 4.3 mL of a 1.38 M solution of DIBAL in hexane. The mixture was allowed to stir at 0  $^\circ\text{C}$  for 40 min and then quenched by dropwise addition of 25 mL of absolute methanol. The mixture was diluted with 50 mL of ether containing 20 mL of methanol and poured into 100 mL of 10% aqueous NaOH solution. The organic phase was washed with three additional portions of 10% aqueous NaOH solution and

(10) Vinylcyclohexene was prepared from cyclohexanone by reaction with vinylmagnesium bromide in THF and distillation of the resulting tertiary allylic alcohol from  $\text{KHSO}_4$ ; see J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

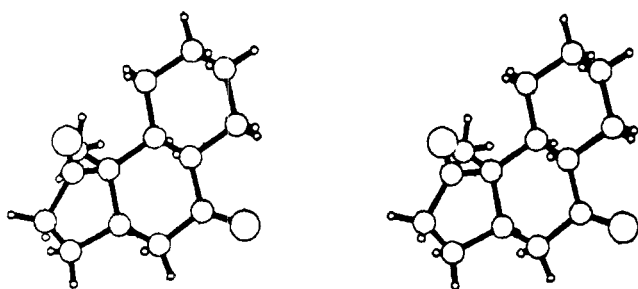


Figure 1. Stereoplot of the tricyclic dione 5.

one portion of saturated aqueous NaCl solution, and dried over  $MgSO_4$ . Removal of solvents under reduced pressure, followed by chromatography over silica gel using 2% ethyl acetate in benzene, gave first 0.92 g (91%) of an alcohol **8a** ( $R_f$  0.26): IR ( $CCl_4$ ) 3600 (m), 1468 (m), 1460 (m), 1445 (m)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.72 (s, 3 H,  $CH_3$ ), 3.83 (br m, 1 H,  $>CHOH$ ), 5.38 (br m, 1 H, vinyl H).

Anal. Calcd for  $C_{14}H_{22}O$ : C, 81.50; H, 10.75. Found: C, 81.32; H, 10.76.

After a few mixed fractions (0.020 g, 2%) there was eluted 0.060 g (6%) of a minor epimeric alcohol: IR ( $CCl_4$ ) 3650 (m), 1480 (m), 1460 (m), 1455 (m)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.95 (s, 3 H,  $CH_3$ ), 3.8 (br m, 1 H,  $>CHOH$ ), 5.2 (br m, 1 H, vinyl H).

Anal. Calcd for  $C_{14}H_{22}O$ : C, 81.50; H, 10.75. Found: C, 81.44; H, 10.90.

**1-(tert-Butyldimethylsilyloxy)-9 $\beta$ -methyl-2,3,3 $\alpha$ ,4,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1H-cyclopenta[*a*]naphthalene (8b).** A mixture of 0.8 g (3.8 mmol) of the alcohol **8b** (major epimer), 1.0 g (14.7 mmol) of sublimed imidazole, 1.2 g (7.9 mmol) of *tert*-butyldimethylsilyl chloride (TBSCl),<sup>6</sup> and 1.6 mL of dry DMF was warmed to 40–45 °C with stirring under an argon atmosphere. After 18 h, 0.57 g (3.8 mmol) of TBSCl and 0.52 g (7.6 mmol) of imidazole were added. After 45 h, 0.29 g (1.9 mmol) of TBSCl and 0.26 g (3.8 mmol) of imidazole were added. After 78 h, the mixture was diluted with ether, washed with a 5% aqueous NaOH solution, water, and saturated aqueous NaCl solution, and dried over  $MgSO_4$ . Removal of solvents under reduced pressure, followed by chromatography over silica gel using cyclohexane afforded 1.18 g (97%) of the silyl ether **8b** as a colorless oil: IR ( $CCl_4$ ) 1480 (m), 1250 (s)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.03 (s, 6 H,  $(CH_3)_2Si$ ), 0.53 (s, 9 H,  $CH_3C$ ), 3.80 (br m, 1 H,  $>CHOSi$ ), 5.2 (br m, 1 H, vinyl H).

Anal. Calcd for  $C_{29}H_{38}OSi$ : C, 74.93; H, 11.32. Found: C, 75.02; H, 11.26.

**1-(tert-Butyldimethylsilyloxy)-5 $\alpha$ -hydroxy-9 $\beta$ -methyl-2,3,3 $\alpha$ ,4,5 $\beta$ ,5 $\alpha$ ,6,7,8,9,9 $\alpha$ ,9 $\beta$ -dodecahydro-1H-cyclopenta[*a*]naphthalene (9).** To a stirred solution of 0.200 g (0.62 mmol) of the silyl ether **8b** in 18 mL of dry THF cooled to 0 °C under an argon atmosphere was added 2.2 mL of a commercial 0.88 M solution of borane-THF. The mixture was allowed to stir at 0 °C for 1 h and at room temperature for 1 h and quenched at 0 °C by careful dropwise addition of 0.5 mL of water. After 10 min at 0 °C, there was added dropwise 1.1 mL of a 30% aqueous  $H_2O_2$  solution and 1.04 mL of a 3 N aqueous NaOH solution simultaneously. The mixture was allowed to stir for 1 h at 0 °C, diluted with 30 mL of water, and extracted three times with ether. The ethereal extracts were washed once with saturated aqueous NaCl solution and dried over  $MgSO_4$ . Removal of solvents under reduced pressure, followed by chromatography over silica gel using 10% ethyl acetate in benzene, gave 0.168 g (79%) of the alcohol **9** as a white crystalline solid: mp 88–90 °C; IR ( $CCl_4$ ) 3650 (w, sh), 3425 (w, br), 1260 (s)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.03 (s, 6 H,  $(CH_3)_2Si$ ), 0.85 (s, 9 H,  $(CH_3)_3C$ ), 1.03 (s, 3 H,  $CH_3$ ), 3.86 (br m, 2 H,  $>CHOR$ ).

An analytical sample was prepared by recrystallization from ether-petroleum ether: mp 89–90 °C.

Anal. Calcd for  $C_{29}H_{38}O_2Si$ : C, 70.94; H, 11.31. Found: C, 71.22; H, 11.22.

**1,5 $\alpha$ -Dihydroxy-9 $\beta$ -methyl-2,3,3 $\alpha$ ,4,5 $\beta$ ,5 $\alpha$ ,6,7,8,9,9 $\alpha$ ,9 $\beta$ -decahydro-1H-cyclopenta[*a*]naphthalene (10).** A solution of 0.150 g (0.44 mmol) of the alcohol silyl ether **9** in 5 mL of methanol containing 4 mL of a 10% aqueous HCl solution was warmed to 70–80 °C for 8 h. The mixture was then diluted with

water and extracted with three portions of ether. The ethereal extracts were washed with saturated NaCl solution and dried over  $MgSO_4$ . Removal of solvents under reduced pressure, followed by chromatography over silica gel using 30% ethyl acetate in benzene, afforded 0.094 g (95%) of the diol **10** as a white crystalline solid: mp 136–137 °C; IR ( $CHCl_3$ ) 3640 (m, sh), 3475 (m, br), 1460 (m, sh)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.12 (s, 3 H,  $CH_3$ ), 3.96 (br m, 2 H,  $>CHOH$ ).

An analytical sample was prepared by recrystallization from ether: mp 137–138 °C.

Anal. Calcd for  $C_{14}H_{24}O_2$ : C, 74.95; H, 10.78. Found: C, 74.77; H, 10.61.

**9 $\beta$ -Methyl-2,3,3 $\alpha$ ,4,5,5 $\alpha$ ,6,7,8,9,9 $\alpha$ ,9 $\beta$ -dodecahydro-1H-cyclopenta[*a*]naphthalene-1,5-dione (11).** To a stirred solution of 0.070 g (0.31 mmol) of the diol **10** in 5 mL of dry dichloromethane was added 0.270 g (1.25 mmol) of pyridinium chlorochromate.<sup>11</sup> After 2 h at room temperature the mixture was diluted with 25 mL of anhydrous ether and filtered through a column of silica gel with 100 mL of anhydrous ether. Removal of solvents under reduced pressure, followed by chromatography on silica gel using 5% ethyl acetate in benzene, afforded 0.057 g (85%) of dione **11** as a white crystalline solid: mp 88–91 °C; IR ( $CCl_4$ ) 1740 (s, sh), 1720 (s, sh), 1460 (m, sh)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.33 (s,  $CH_3$ ).

An analytical sample was prepared by recrystallization from cyclohexane: mp 41–42 °C.

Anal. Calcd for  $C_{14}H_{20}O_2$ : C, 76.33; H, 9.15. Found: C, 76.29; H, 9.16.

**Conversion of the Dione 11 to the Dione 5.** To a stirred solution of 0.050 g (0.23 mmol) of the dione **11** in 10 mL of dry methanol was added 0.05 mL of a 0.54 M stock solution of sodium methoxide in methanol. The mixture was gently refluxed for 15 min, diluted with ether, washed with saturated NaCl solution, and dried over  $MgSO_4$ . Removal of solvents under reduced pressure, followed by chromatography over silica gel using 5% ethyl acetate in benzene, afforded 0.047 g (95%) of the crystalline dione **5**: mp 74–76 °C; IR ( $CCl_4$ ) 1740 (s, sh), 1460 (m)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.18 (s,  $CH_3$ ).

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**Registry No.** 2, 1120-73-6; 3, 71096-87-2; 4, isomer 1, 71096-88-3; 4, isomer 2, 71096-89-4; 5, 71096-90-7; 6, 2622-21-1; 7, 71096-91-8; 8a, isomer 1, 71096-92-9; 8a isomer 2, 71096-93-0; 8b, 71096-94-1; 9, 71096-95-2; 10, 71096-96-3; 11, 71096-97-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; acetylcyclohexene, 932-66-1.

**Supplementary Material Available:** The atom numbering system used (Figure 2); additional plots including a view of packing in the unit cell (Figure 3); positional and thermal parameters (Table I); and bond distances and torsional angles (Table II) (18 pages). Ordering information is given on any current masthead page.

(11) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).

### $\beta$ -Lithioenamines from $\beta$ -Chloroamine. A Convenient Preparation Method of Hindered Ketones

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We have recently reported that the reaction of alkyl-lithium reagents with  $\beta$ -bromoenamines produces  $\beta$ -lithioenamines by a halogen-metal exchange reaction.<sup>1</sup> In