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Rearrangement of Bis[(2,4,6-Trimethylphenyl)methanoyl]bicyclo[2.2.1]hept-5-enes to 2-Oxabicyclo[3.3.0]octa-3,7-dienes[1]

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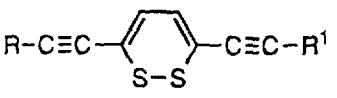
Abstract: 2-*endo*-3-*endo*- and 2-*endo*-3-*exo*-bis(2,4,6-trimethylphenyl)]methanoylbicyclo-[2.2.1]hept-5-ene (**6** and **7**) rearrange in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and bis(trimethylsilyl) sulfide to 3-(2,4,6-trimethylphenyl)-4-[(2,4,6-trimethylphenyl)methyl]-2-oxabicyclo[3.3.0]octa-3,7-diene (**8**) and 3-(2,4,6-trimethylphenyl)-4-[(*Z*-1-(2,4,6-trimethylphenyl)-1-(trimethylsiloxy)ethenyl]-2-oxabicyclo[3.3.0]octa-3,7-diene (**9**). No reaction occurs under these experimental conditions with 2-*endo*-3-*endo*- and 2-*endo*-3-*exo*-bis[(2,4,6-trimethylphenyl)methanoyl]bicyclo[2.2.1]heptane (**10** and **11**).

During our studies of the synthesis and bioactivity of thiarubrines (1,2-dithia-3,5-hexadienes, 1,2-dithiins, **1**),[2-7] it was observed that the attempted trimethylsilyl trifluoromethanesulfonate (TMSOTf) promoted bis(trimethylsilyl) sulfide sulfurization of the bicyclic 1,4-diketones **2** and **3**[9-12] led to the 5-aroyl-3-aryl-2-thiabicyclo[4.3.0]nona-3,8-dienes **4** and **5** via a thia-Cope rearrangement.[6] Under the same experimental conditions, 2-*endo*-3-*endo*- and 2-*endo*-3-*exo*-bis(2,4,6-trimethylphenyl)]methanoylbicyclo[2.2.1]hept-5-ene (**6** and **7**) underwent a rearrangement to 3-(2,4,6-trimethylphenyl)-4-[(2,4,6-trimethylphenyl)methyl]-2-oxabicyclo[3.3.0]octa-3,7-diene (**8**) and 3-(2,4,6-trimethylphenyl)-4-[(*Z*-1-(2,4,6-trimethylphenyl)-1-(trimethylsiloxy)ethen-yl]-2-oxabicyclo[3.3.0]octa-3,7-diene (**9**). No products were isolated from **6** or **7** when only TMSOTf, only bis(trimethylsilyl) sulfide, or only trifluoromethanesulfonic acid was used. In the absence of a carbon-carbon double bond, 2-*endo*-3-*endo*- or 2-*endo*-3-*exo*-bis[(2,4,6-trimethylphenyl)methanoyl]bicyclo[2.2.1]heptane (**10** or **11**) did not undergo rearrangement in the presence of TMSOTf and bis(trimethylsilyl) sulfide, only bis(trimethylsilyl) sulfide, or only trifluoromethanesulfonic acid.



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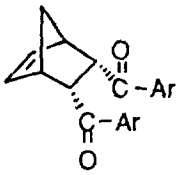
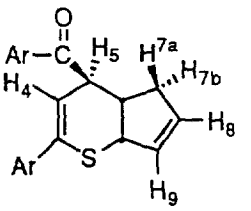
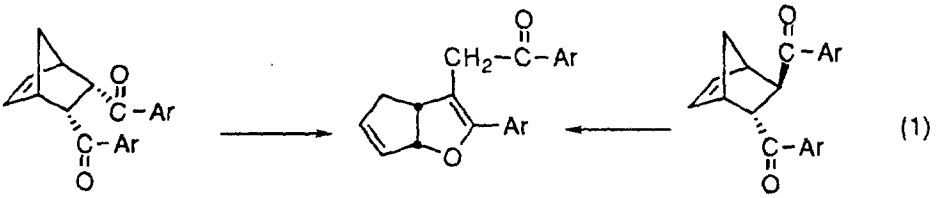


2 Ar = C_6H_5
3 Ar = 4-$CH_3C_6H_4$

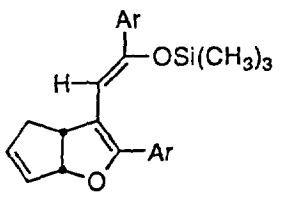


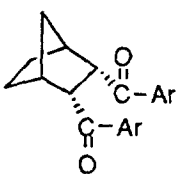
4 Ar = C_6H_5
5 Ar = 4-$CH_3C_6H_4$

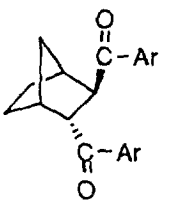


(1)

6 Ar = 2,4,6-$(CH_3)_3C_6H_2$ 8 Ar = 2,4,6-$(CH_3)_3C_6H_2$ 7 Ar = 2,4,6-$(CH_3)_3C_6H_2$

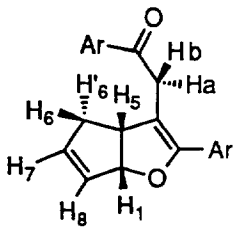




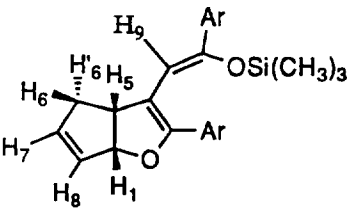


9 Ar = 2,4,6-$(CH_3)_3C_6H_2$ 10 Ar = 2,4,6-$(CH_3)_3C_6H_2$ 11 Ar = 2,4,6-$(CH_3)_3C_6H_2$

The molecular structures of **8** and **9** were established with the aid of ^1H, ^{13}C, DEPT, and ^1H-^1H COSY NMR spectra. In compound **8**, the coupling constant (J = 16.8 Hz, J = 18.6 Hz) indicated that two methylene groups (CH_2) should be in the molecule, which was supported by a DEPT experiment. Protons Ha and Hb showed a typical AB-type coupling pattern (two doublet signals). This AB-type coupling pattern was not seen in the ^1H NMR spectrum of compound **9**. Instead, a singlet signal was found at 4.75 ppm, which is indicative of a vinyl proton.



8



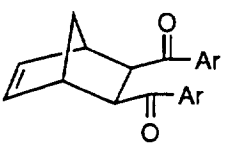
9

^1H-^1H NOE difference spectroscopy was used to determine the configurations of bicycles **8** and **9**. In both **8** and **9**, a cis fusion of the two five-membered rings was apparent because of the strong positive enhancement for H1 (+11.4%) upon the irradiation of H5. In compound **9**, observation of a positive NOE from H9 to Ar-CH_3 (~ +1.8%) indicated a close proximity of H9 and the 2,4,6-trimethylphenyl group.

Compounds **6** and **7** could be resistant to the mild thionation procedure[8,13] owing to steric hindrance at the carbonyl group. It appears that the two highly reactive reagents TMSOTf and bis(trimethylsilyl) sulfide both play roles in the reaction.[8,13] The combination of TMSOTf and bis(trimethylsilyl) sulfide catalyzes rearrangement of **6** and **7** to **8** and **9**.[14-19] The lack of reactivity of **10** and **11** suggests that the double bond is involved in the mechanism.

The products of the rearrangement reactions could be potentially useful for the synthesis of derivatives of biologically active molecules.[19-29]

2-*exo*-3-*exo* -Bis(2,4,6-trimethylphenyl)bicyclo[2.2.1]hept-5-ene (**12**) was isolated as the minor product during the preparation of **6** from (Z)-1,4-bis(2,4,6-trimethylphenyl)but-2-ene-1,4-dione and cyclopentadiene.[9-12]



12 Ar = 2,4,6-$(CH_3)_3C_6H_2$

EXPERIMENTAL

General. Microanalyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ 07940. EIMS were obtained at an ionization potential of 70 eV and CIMS (2-methylpropane) were obtained at 50, 70, or 100 eV. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded in $CDCl_3$. Analytical TLC was performed on Analtech Uniplate 10 x 20 cm (250 μ thick) silica gel GF prescored glass plates, which were developed with hexanes or 10:1 hexanes/ethyl acetate. The plates were visualized by UV. Flash column chromatography was performed on 225-400 mesh silica gel.

(*E*)-1,4-Bis(2,4,6-Trimethylphenyl)but-2-ene-1,4-dione was prepared (36%) as previously described:[9a] yellow crystals, mp 176.5-177 °C [lit.[9a] mp 174 °C]; TLC 10:1 hexanes/ethyl acetate, R_f = 0.58; HREIMS *m/z* 320.1772, calcd 320.1776 for $C_{22}H_{24}O_2$; IR (KBr, cm^{-1}) 2917 m, 1665 s, 1610 m, 1436 m; ^{1}H NMR δ 6.86 (s, 4 H), 6.68 (s, 2 H), 2.29 (s, 6 H), 2.13 (s, 12 H); ^{13}C NMR δ 19.38, 21.10, 128.59, 128.62, 128.65, 128.69, 134.07, 135.83, 139.38, 140.97, 201.59.

(Z)-1,4-Bis(2,4,6-Trimethylphenyl)but-2-ene-1,4-dione was prepared (67%) by photolysis[11,12] of (*E*)-1,4-bis(2,4,6-trimethylphenyl)but-2-ene-1,4-dione: white crystals, mp 119-120.5 °C; TLC 10:1 hexanes/ethyl acetate, R_f = 0.49; HREIMS *m/z* 320.1774, calcd 320.1776 for $C_{22}H_{24}O_2$; IR (KBr, cm^{-1}) 2920 m, 1670 s, 1615 m, 1440 m; ^{1}H NMR δ 6.81 (s, 4 H), 6.60 (s, 2 H), 2.32 (m, 18 H); ^{13}C NMR δ 18.42, 19.31, 127.28, 133.96, 134.51, 134.88, 137.90, 196.57. Anal. calcd for $C_{22}H_{24}O_2$: C, 82.45; H, 7.55. Found: C, 82.60; H, 7.50.

Preparation of 2-*endo*-3-*endo*-Bis(2, 4, 6-Trimethylphenyl)bicyclo[2.2.1]hept-5-ene (6). (*Z*)-1,4-Bis(2, 4, 6-trimethylphenyl)but-2-ene-1,4-dione and cyclopentadiene were used to prepare **6**:[11,12] red crystals (72%); mp 182-183.5 °C; TLC 10:0.5 hexanes/ethyl acetate, R_f = 0.34; HRCIMS *m/z* [M+H]$^+$ 387.2339, calcd 387.2324 for ($C_{27}H_{30}O_2$ + H$^+$); ^{1}H NMR δ 6.84 (s, 4 H), 6.03 (s, 2 H), 3.87 (s, 2 H), 3.10 (s, 2 H), 2.37 (s, 12 H), 2.33 (s, 6 H), 1.43 (d, 2 H); ^{13}C NMR δ 18.24, 19.33, 45.40, 47.73, 57.32, 127.15, 127.17, 132.43, 133.86, 136.65, 137.98, 205.21. Anal. calcd for $C_{27}H_{30}O_2$: C, 83.89; H, 7.83. Found: C, 83.84; H, 7.83. **2-*exo*-3-*exo*-Bis(2, 4, 6-Trimethylphenyl)bicyclo[2.2.1]hept-5-ene (12)** was also isolated: mp 164-165 °C; TLC 10:0.5 hexanes/ethyl acetate, R_f = 0.41; HREIMS *m/z* 386.2252, calcd 386.2245 for $C_{27}H_{30}O_2$; ^{1}H NMR δ 6.86 (s, 4 H), 6.21 (s, 2 H), 3.16 (d, 2 H), 3.02 (s, 2 H), 2.37 (s, 12 H), 2.33 (s, 6 H), 2.29 (d, 1 H), 1.38 (d, 1 H) ; ^{13}C NMR δ 20.22, 21.04, 44.26, 46.21, 56.68, 129.11, 134.64, 138.45, 138.66, 138.74, 207.19. Anal. calcd for $C_{27}H_{30}O_2$: C, 83.89; H, 7.83. Found: C, 83.68; H, 7.89.

Preparation of 2-*endo*-3-*exo*-Bis(2, 4, 6-Trimethylphenyl)bicyclo[2.2.1]hept-5-ene (7). (*E*)-1,4-Bis(2, 4, 6-trimethylphenyl)but-2-ene-1,4-dione and cyclopentadiene were used to prepare **7**:[11,12] red crystals (77%); mp 115-116 °C; TLC 10:1 hexanes/ethyl acetate, R_f = 0.54; HREIMS

m/z 386.2238, calcd 386.2245 for $C_{27}H_{30}O_2$; IR (KBr, cm^{-1}) 2975 s, 1683 s, 1560 m, 1448 m; ^1H NMR δ 6.82 (d, 4 H), 6.21 (q, 2 H), 4.37 (q, 1 H), 3.30 (s, 1 H), 3.26 (d, 1 H), 2.99 (s, 1 H), 2.27 (d, 6 H), 2.20 (s, 6 H), 2.03 (s, 6 H); ^{13}C NMR δ 17.70, 18.02, 18.04, 19.26, 19.32, 44.00, 45.05, 45.15, 53.34, 54.92, 127.03, 127.11, 131.62, 131.94, 135.07, 135.11, 135.15, 136.70, 136.80, 136.93, 137.13, 206.70, 208.53. Anal. calcd for $C_{27}H_{30}O_2$: C, 83.89; H, 7.83. Found: C, 83.85; H, 7.68.

Preparation of 3-(2,4,6-Trimethylphenyl)-4-[(2,4,6-trimethylphenyl)methyl]-2-oxabicyclo[3.3.0]octa-3,7-diene (8) and 3-(2,4,6-Trimethylphenyl)-4-[(*Z*-1-(2,4,6-trimethylphenyl)-1-(trimethylsiloxy)ethenyl]-2-oxabicyclo[3.3.0]octa-3,7-diene (9). To a solution of bis(trimethylsilyl) sulfide (238 mg, 1.32 mmol), trimethylsilyl trifluoromethansulfonate (TMSOTf, 29 mg, 0.13 mmol) in acetonitrile (10 mL, refluxed with CaH_2 and distilled), 2-*endo*-3-*endo*-bis(2,4,6-trimethylphenyl)bicyclo[2.2.1]hept-5-ene (255 mg, 0.66 mmol, **6**) was added in 10 min *via* a solid addition funnel. The mixture was stirred at rt under N_2 for 3 h. The reaction progress was monitored by TLC. Diethyl ether (50 mL) was added and the solution was washed with 8% cold $NaHCO_3$ (30 mL), saturated NaCl solution (50 mL) and dried ($MgSO_4$). The solution was concentrated *in vacuo* and the residue was chromatographed (95:5 hexanes/ethyl acetate) to give **8** and **9**.

Compound **8** (yellow oil, 25 mg, 16%); TLC 10:2 hexanes/ethyl acetate, $Rf = 0.24$; HRCIMS *m/z* $[M + H]^+$ 387.2316, calcd 387.2324 for $[C_{27}H_{30}O_2 + H^+]$; ^1H NMR δ 2.04 (d, J = 14.8 Hz, 6 H, two CH_3), 2.23 (d, J = 10.1 Hz, 12 H, four CH_3), 2.45 (d, J_{gem} = 16.8 Hz, H'-6), 2.60 (dd, J_{gem} = 16.8 Hz, J = 7.8 Hz, H-6), 3.09 (d, J_{gem} = 18.6 Hz, H-a methylene), 3.17 (d, J_{gem} = 18.6 Hz, H-b methylene), 4.04 (t, J = 8.6 Hz, H-5), 5.70 (d, J = 8.6 Hz, H-1), 5.84 (dd, J = 2.1 Hz, J = 5.5 Hz, H-7), 6.05 (dd, J = 2.1 Hz, J = 3.1 Hz, H-8), 6.74 (d, J = 10.1 Hz, Ph-H); ^{13}C NMR δ 16.96 (CH_3), 17.25 (CH_3), 17.62 (CH_3), 19.20 (CH_3), 19.32 (CH_3), 35.42 (CH_2), 39.58 (CH_2), 44.44 (C-5), 88.08 (C-1), 104.52, 125.49, 126.06, 126.14, 126.61, 128.28, 130.71, 132.52, 135.87, 136.39, 136.41, 136.45, 137.75, 148.07, 206.01 (C=O). Anal. calcd for $C_{27}H_{30}O_2$: C, 83.89; H, 7.83. Found: C, 83.74; H, 7.77.

Compound **9** (yellow oil, 80 mg, 20%); TLC 10:2 hexanes/ethyl acetate, $Rf = 0.36$; HREIMS *m/z* 458.2643, calcd 458.2641 for $C_{27}H_{29}O_2Si(CH_3)_3$; ^1H NMR δ 0.01 (s, $Si(CH_3)_3$, 9 H), 2.22-2.35 (m, Ph-CH_3, 18 H), 2.71 (d, J_{gem} = 17.6 Hz, H'-6), 2.80 (dd, J gem = 17.6 Hz, J = 7.8 Hz, H-6), 4.28 (t, J = 8.6 Hz, H-5), 4.75 (s, H-9), 5.68 (d, J = 8.6 Hz, H-1), 5.88 (m, J = 1.8 Hz, J = 6.8 Hz, H-7), 6.12 (d, J = 6.8 Hz, H-8), 6.79 (m, Ph-H, 4 H); ^{13}C NMR δ 18.45, 18.79, 19.24, 19.32, 39.20, 44.26, 88.17, 103.77, 111.85, 125.89, 126.14, 126.25, 126.33, 127.84, 133,68, 134.10, 135.26, 135.40, 136.05, 136.11.

Thionation of 2-*endo*-3-*exo*-Bis(2,4,6-Trimethylphenyl)bicyclo[2.2.1]hept-5-ene (7). Treatment of **7** with TMSOTf and bis(trimethyl)silyl sulfide as described above for compound **6** afforded **8** (4%) and **9** (20%).

Preparation of 2-*endo*-3-*endo*-bis[(2,4,6-trimethylphenyl)methanoyl]bicyclo[2.2.1]heptane (10). Hydrogenation[6] of compound **6** afforded **10** (98%) : mp 213-214.5 °C; TLC 10:0.5 hexanes/ethyl acetate, R_f = 0.36; HRCIMS *m/z* [M + H]$^+$ 389.2477, calcd 389.2480 for ($C_{27}H_{32}O_2 + H^+$); ^{1}H NMR δ 6.84 (s, 4 H), 3.53 (s, 2 H), 2.49 (s, 2 H), 2.40 (s, 12 H), 2.27 (s, 6 H), 1.74 (d, 2 H), 1.56 (d, 2 H), 1.46 (d, 1 H), 1.32 (d, 1 H); ^{13}C NMR δ 19.96, 20.04, 21.02, 24.11, 41.04, 41.11, 56.46, 128.89, 128.97, 134.18, 138.27, 139.60, 207.60. Anal. calcd for $C_{27}H_{32}O_2$: C, 83.45; H, 8.31. Found: C, 83.24; H, 8.10.

Preparation of 2-*endo*-3-*exo*-bis[(2,4,6-trimethylphenyl)methanoyl]bicyclo[2.2.1]heptane (11). Hydrogenation[6] of compound **7** gave **11** (99%): mp 145.0-146.5 °C; TLC 10:0.5 hexanes/ethyl acetate, R_f = 0.45; HRCIMS *m/z* [M + H]$^+$ 389.2489, calcd 389.2480 for ($C_{27}H_{32}O_2 + H^+$); ^{1}H NMR δ 6.83 (d, 4 H), 4.22 (m, 1 H), 3.39 (d, 1 H), 2.68 (s, 1 H), 2.42 (d, 1 H), 2.27 (d, 6 H), 2.23 (s, 6 H), 2.11 (s, 6 H), 1.65 (m, 1 H), 1.54 (m, 2 H), 1.45 (m, 2 H), 1.30 (dd, 1 H); ^{13}C NMR δ 17.95, 19.26, 19.33, 22.19, 28.66, 36.47, 38.67, 39.65, 53.67, 55.25, 127.08, 127.12, 131.68, 136.68, 136.86, 137.74, 206.99, 209.06. Anal. calcd for $C_{27}H_{32}O_2$: C, 83.45; H, 8.31. Found: C, 83.40; H, 8.14.

Attempted Reactions of 2-*endo*-3-*endo*-bis[(2,4,6-trimethylphenyl)methanoyl]-bicyclo[2.2.1]heptane (10) and 2-*endo*-3-*exo*-bis[(2,4,6-trimethylphenyl)methanoyl]bicyclo[2.2.1]heptane (11). No product was isolated from the treatment of **10** and **11**, respectively, with TMSOTf and bis(trimethylsilyl) sulfide, with only TMSOTf, and with only bis(trimethylsilyl) sulfide as described above for compounds **6** and **7**.

ACKNOWLEDGMENTS

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