1162, 1090, 1047, cm^{-1}; ^{1}H NMR (90 MHz) δ 0.06 (s, 6 H), 0.85 (s, 12 H), 0.89 (d, J = 7.1 Hz 3 H), 1.17 (s, 6 H), 4.07 (br s, 1 H); MS m/z 381 (M$^+$ - Me, 2.4), 191 (25), 173 (60), 135 (42), 109 (35), 95 (47), 81 (36), 75 (100); exact mass calcd for $C_{23}H_{45}O_2Si$ (M$^+$ - Me) 381.3189, found 381.3225. Anal. Calcd for $C_{24}H_{48}O_2Si$: C, 72.66; H, 12.21. Found: C, 72.58; H, 12.03.

[1*R*-[1β(*R),3aα,4β,7aβ]]-Octahydro-4(*E*)-(2-oxoethylidene)-1-[5-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-1,5-dimethylhexyl]-7a-methyl-1*H*-indene (3).** To a stirred solution of alcohol **7** (525 mg, 1.33 mmol) in CH_2Cl_2 (35 mL) at room temperature was added pyridinium chlorochromate (875 mg, 3.98 mmol). After 1 h, the reaction mixture was diluted with Et_2O and filtered through Florisil. The filtrate was evaporated to leave ketone **8** (520 mg) as a yellow oil, which was used without purification.

To a stirred solution of lithium diisopropylamide (3.50 mmol) in THF (10 mL) at 0 °C was added a solution of *N*-*tert*-butyl-2-(trimethylsilyl)acetaldimine[7a] (544 mg, 3.18 mmol). After 20 min, this mixture was cooled to -78 °C, and a solution of crude **8** (520 mg) in THF (7 mL) was then added. The resulting mixture was permited to warm to -20 °C, stirred for 30 min, and then quenched with 5% oxalic acid (18 mL). After stirring for 1.5 h at room temperature, the reaction mixture was extracted with Et_2O. The extract was washed with water and saturated $NaHCO_3$, dried, concentrated, and chromatographed on silica gel (1:40 Et_2O-hexane) to give aldehyde **3** (486 mg, 88%) as a colorless viscous oil: $[\alpha]^{29}_D$ +102.1° (*c* 1.064, $CHCl_3$); IR (neat) 1675, 1634, 1470, 1380, 1362, 1250, 1044 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.06 (s, 6 H), 0.60 (s, 3 H), 0.85 (s, 12 H), 0.93 (d, J = 5.9 Hz, 3 H), 1.18 (s, 6 H), 3.37 (dd, J = 10.9 and 2.9 Hz, 1 H), 5.73 (dd, J = 8.3 and 1.5 Hz, 1 H), 10.07 (d, J = 8.3 Hz, 1 H); MS m/z 405 (M$^+$ - Me, 3.3), 363 (22), 271 (24), 173 (48), 159 (17), 133 (20), 109 (15), 95 (16), 81 (17), 75 (100); exact mass calcd for $C_{25}H_{45}O_2Si$ (M$^+$ - Me) 405.3189, found 405.3163. Anal. Calcd for $C_{26}H_{48}O_2Si$: C, 74.23; H, 11.51. Found: C, 74.40; H, 11.69.

Cr(II)-Mediated Coupling Reaction of 2 and 3. To a stirred suspension of $LiAlH_4$ (54 mg, 1.43 mmol) in THF (8 mL) at 0 °C was added $CrCl_3$ (453 mg, 2.86 mmol), and the mixture was stirred at 0 °C for 10 min and then at room temperature for 30 min. The resulting black suspension was recooled to 0 °C, and a mixture of **2** (230 mg, 0.48 mmol) and **3** (300 mg, 0.71 mmol) in THF (5 mL) was added. After stirring at 0 °C for 10 min and at room temperature for 45 min, the reaction mixture was quenched with water, diluted with Et_2O, and filtered through Celite to remove the inorganic precipitates. The organic layer of the filtrate was washed with saturated NaCl and then dried. Removal of the solvent left a yellow oil (504 mg) which was reduced with DIBAL as follows in order to simplify purification of **9**. To a stirred solution of the above crude mixture in CH_2Cl_2 (6 mL) at -50 °C was added 1 M DIBAL in CH_2Cl_2 (2 mL, 2 mmol), and stirring was continued at -50 °C for 30 min. The reaction mixture was quenched with 1 N NaOH (1 mL), allowed to warm to room temperature, and stirred for an additional 30 min. The resulting sludge was removed by filtration through Celite and thoroughly washed with CH_2Cl_2. The combined filtrates were dried, concentrated, and chromatographed on silica gel. Elution with 1:40 Et_2O-hexane gave alcohol **9** (307 mg, 83%) as a colorless viscous oil: $[\alpha]^{29}_D$ +29.8° (*c* 0.646, $CHCl_3$); IR (neat) 3420, 1470, 1363, 1382, 1255, 1105, 1080, 1040, 1005 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.06 (s, 6 H), 0.07 (s, 3 H), 0.08 (s, 3 H), 0.10 (2 s, 6 H), 0.56 (s, 3 H), 0.85 (s, 9 H), 0.90 (s, 9 H), 0.91 (s, 12 H), 0.93 (d, J = 6.7 Hz, 3 H), 1.17 (s, 3 H), 1.18 (s, 3 H), 2.53 (q, J = 5.5 Hz, 1 H), 2.62 (br d, J = 11.6 Hz, 1 H), 3.50 (br s, 1 H, exchangeable with D_2O), 4.23 (m, 1 H), 4.58 (dd, J = 4.9 and 8.5 Hz, 1 H), 4.66 (br dd, J = 7.3 and 4.3 Hz, 1 H), 4.82 (s, 1 H), 5.05 (d, J = 8.5 Hz, 1 H), 5.10 (s, 1 H); MS m/z 758 (M$^+$ - H_2O, 3) 626 (20), 569 (10), 494 (5), 379 (10), 356 (9), 355 (9), 299 (10), 289 (12), 271 (8), 248 (18), 167 (37), 147 (11), 133 (10), 109 (9), 95 (14), 93 (14), 81 (12), 75 (100); exact mass calcd for $C_{45}H_{86}O_3Si_3$ (M$^+$ - H_2O) 758.5885, found 758.5908. Further elution with 1:6 Et_2O-hexane gave alcohol **10** (67 mg, 67% based on the excess of **3**) as a colorless oil: $[\alpha]^{29}_D$ +49.1° (*c* 0.978, $CHCl_3$); IR (neat) 3360, 1466, 1364, 1382, 1255, 1150, 1042 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.06 (s, 6 H), 0.56 (s, 3 H), 0.85 (s, 12 H), 0.92 (d, J = 6.4 Hz, 3 H), 1.18 (s, 6H), 2.65 (br dd, J = 10.0 Hz and 2.8 Hz, 1 H), 4.20 (d, J = 7.3 Hz, 2 H), 5.22 (t, J = 7.3 Hz, 1 H); MS m/z 407 (M$^+$ - Me, 4), 273 (23), 217 (66), 173 (59), 161 (28), 149 (16), 135 (29), 121 (26), 109 (27), 95 (31), 81 (31), 75 (100); exact mass calcd for $C_{25}H_{47}O_2Si$ (M$^+$ - Me) 407.3345, found 407.3334.

Oxidation of this alcohol **10** (30 mg, 0.07 mmol) with activated MnO_2 (300 mg) in CH_2Cl_2 (5 mL) at room temperature for 1 h gave practically pure starting aldehyde **3** (29.6 mg, 99%).

1α,25-Dihydroxyvitamin D$_3$ (1). A mixture of alcohol **9** (66.6 mg, 0.09 mmol) and $CuSO_4$ on SiO_2 (3.14 mmol/g) (30 mg, 0.09 mmol) in benzene (10 mL) was heated at 50 °C for 1.5 h. After cooling to room temperature, the reaction mixture was filtered through Celite, and the catalyst was thoroughly washed with Et_2O. The combined filtrates were evaporated to dryness to give a yellow viscous oil (65.3 mg). The residue was dissolved in a mixture of 46% HF (1 mL), MeOH (2 mL), and THF (2 mL). After being stirred at room temperature for 5 h, the reaction mixture was basified with saturated $NaHCO_3$, extracted with CH_2Cl_2, dried, and concentrated. Purification by preparative TLC developed twice with Et_2O afforded 1α,25-dihydroxyvitamin D$_3$ (**1**) (11.6 mg, 33%) and **14** (20.4 mg, 57%).

1α,25-Dihydroxyvitamin D$_3$ (**1**) was obtained as the less polar component, colorless plates (recrystallized from methyl formate): mp 117-118 °C (lit.[10] mp 118-119 °C); $[\alpha]^{29}_D$ +47.8° (*c* 1.00, EtOH) [lit.[10] $[\alpha]^{29}_D$ +47.9° (*c* 0.5, EtOH)]; IR (Nujol) 3290, 1143, 1072, 1055, 905 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$ + CD_3OD) δ 0.54 (s, 3 H), 0.94 (d, J = 6.1 Hz, 3 H), 1.20 (s, 6 H), 2.30 (dd, J = 13.4 and 6.7 Hz, 1 H), 2.56 (dd, J = 13.4 and 3.7 Hz, 1 H), 2.83 (dd, J = 12.8 and 4.0 Hz, 1 H), 4.17 (m, 1 H), 4.39 (dd, J = 8.0 and 4.9 Hz), 4.99 (s, 1 H), 5.32 (s, 1 H), 6.06 (d, J = 11.0 Hz, 1 H), 6.36 (d, J = 11.0 Hz, 1 H); MS m/z 416 (M$^+$, 5), 398 (9), 380(7), 285 (5), 174 (7), 159 (10), 152 (20), 134 (100), 119 (11), 105 (24); exact mass calcd for $C_{27}H_{44}O_3$ (M$^+$) 416.3290, found 416.3328. These spectral data are in accord with those reported.[10]

The more polar isomer (**14**) was obtained as a colorless amorphous solid: $[\alpha]^{29}_D$ +92.3° (*c* 1.285, EtOH); IR (neat) 3390, 1650, 1600, 1460, 1375, 1260, 1210, 1050, 1030, 970, 905 cm^{-1}; NMR (500 MHz) δ 0.90 (s, 3 H), 0.97 (d, J = 6.7 Hz, 3 H), 1.24 (s, 6 H), 3.22 (m, 1 H), 4.27 (m, 1 H), 4.50 (t, J = 3.4 Hz, 1 H), 4.79 (s, 1 H), 4.96 (s, 1 H), 5.55 (dd, J = 15.9 and 7.9 Hz, 1 H), 6.32 (d, J = 15.9 Hz, 1 H); MS m/z 416 (M$^+$, 3), 398 (3), 167 (43), 149 (100), 123 (28), 113 (17), 99 (26); exact mass calcd for $C_{27}H_{44}O_3$ (M$^+$) 416.3290, found 416.3270.

Supplementary Material Available: ^{1}H NMR spectra for **1**, **3**, **9**, **10**, and **14** (17 pages). Ordering information is given on any current masthead page.

Novel Rearrangement of 8-Methyltricyclo[6.4.0.0^{1,4}]dodecan-5-ones to Angularly Fused and Spiro-Annulated Tricyclic Ketones

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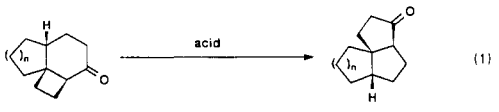
Recently we reported that 5,6-disubstituted bicyclo[4.2.0]octan-2-ones such as **1** rearrange under the action of acid catalysts through a new pathway to give bicyclo[3.3.0]octanones such as **2** (eq 1).[1] Total syntheses of some



(1)

1 n = 1, 2, 3 2

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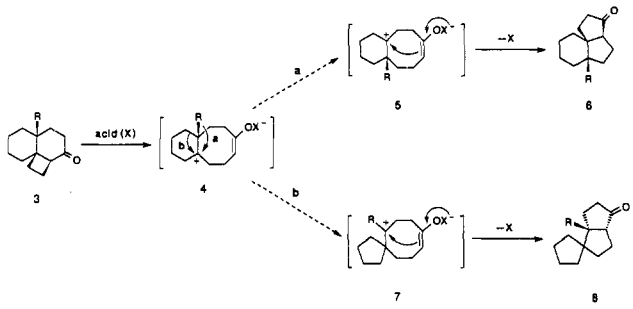
0022-3263/91/1956-0463$02.50/0

Scheme I



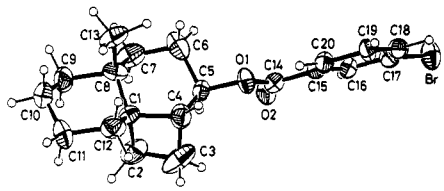
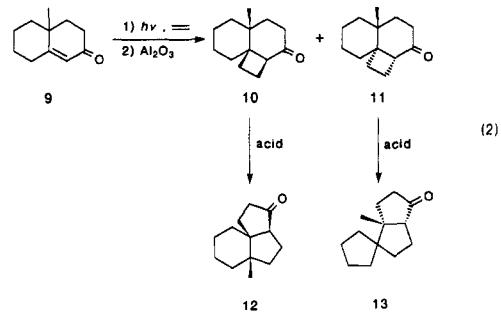


Figure 1. Molecular structure of *m*-bromobenzoate **14**.

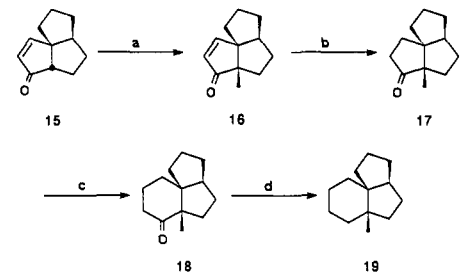
angularly fused triquinane natural products have been achieved by utilizing this rearrangement as the pivotal step.[1b,2] We also proposed the mechanism that involves the fission of the central cyclobutane bond to generate a homoallylcarbinyl cation such as **4** (R = H) shown in Scheme I followed by the 1,2-hydride shift and subsequent transannular cyclization of a cation such as **5**.[1b] It is anticipated that, in the cation **4** derived from ketone **3** having an alkyl group at C(8) position (R = alkyl), two modes of migration are available (Scheme I). One involves a 1,2-alkyl shift of the R group (path a) to generate tertiary cation **5**, which cyclizes to give **6** with an angular alkyl group. The other mode involves an alkyl shift of the tetramethylene group (path b) to form tertiary cation **7** and subsequent cyclization leads to a novel spiro-annulated ring system such as **8**. From this viewpoint, we have studied the acid-catalyzed rearrangement of (1*R**,4*S**,8*R**)- and (1*S**,4*R**,8*R**)-8-methyltricyclo[6.4.0.0^{1,4}]dodecan-5-ones (**10** and **11**) and found that while **10** gave the angularly fused ketone **12**, **11** produced the unique spiro-annulated ketone **13** (eq 2).



(2)

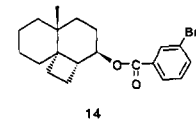
Tricyclic ketones **10** and **11** were prepared in 14% and 63% yields by photocycloaddition of ethylene to the known bicyclic enone **9**[3] followed by column chromatography on alumina, which effected equilibrium from the trans 6-4 ring system to the more stable cis 6-4 ring system.[4] *m*-

Scheme II[a]



[a] (a) LDA, MeI; (b) H_2, Pd/C; (c) (i) LDA, TMSCl; (ii) Et_2Zn, CH_2I_2; (iii) $FeCl_3$, Pyr; (iv) AcONa; (v) H_2, Pd/C; (d) N_2H_4, KOH.

Bromobenzoate **14** was prepared from **11** by reduction followed by esterification in order to determine the stereochemistry of **10** and **11**. A single-crystal X-ray analysis of **14** (Figure 1) revealed that it has 1*S**,4*R**,8*R** stereochemistry (cis–trans relationship between the three rings). Therefore, **11** is cis,trans isomer and **10** had cis,cis stereochemistry (1*R**,4*S**,8*R**).



Reaction of the cis,cis ketone **10** with 2 equiv of $AlCl_3$ in CH_2Cl_2 gave the angularly fused tricyclic ketone **12** in 71% yield, having a methyl group at C(8). The structure was elucidated from spectroscopic data and the identity of hydrocarbon **19** derived by Wolff–Kishner reduction of **12** with an authentic sample prepared independently as shown in Scheme II. C(5)-Methylation of the angularly fused triquinane enone **15**[5] gave the ketone **16** as a single product having the methyl group with 5*S** stereochemistry.[6] Hydrogenation of **16** and subsequent ring expansion of **17** gave 6-5-5 fused ketone **18**, which was reduced to afford **19**. An experiment using the C(6) monodeuterated derivative of ketone **10** was undertaken as described previously[1] in order to establish whether **12** was formed by the novel pathway or the Cargill rearrangement.[7] It revealed that the rearrangement occurred via path a, which involves migration of the methyl group in the homoallylcarbinyl cation **4** (R = CH_3) as shown in Scheme I.

Similar reaction of cis,trans ketone **11** gave **12** in 9% yield. Interestingly, the major product was the spiro-annulated triquinane ketone **13** (70% yield).[8] The novel structure of **13** was unambiguously determined by the 2D ^{13}C-INADEQUATE spectrum (100 MHz) shown in Figure 2. Moreover, with concentrated H_2SO_4 (ca. 4 equiv) in benzene only **13** was obtained in 77% yield. The labeling experiment as described above showed that the relationship between the deuterium and the carbonyl group was maintained during rearrangement. Accordingly, it is reasonable to consider that the main pathway involves a 1,2-alkyl shift of the tetramethylene group, i.e., C(8)–C(9) bond (path b, R = CH_3) in the homoallylcarbinyl cation **4** derived from **11** and the subsequent cyclization to give

(1) (a) Ue, M.: Tsukahara, H.; Kobiro, K.; Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1987**, *28*, 3979. (b) Kakiuchi, K.; Ue, M.; Tsukahara, H.; Simizu, T.; Miyao, T.; Tobe, Y.; Odaira, Y.; Yasuda, M.; Shima, K. *J. Am. Chem. Soc.* **1989**, *111*, 3707.

(2) Ue, M.: Ohnishi, Y.: Kobiro, K.; Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Chem. Lett.* **1990**, 149.

(3) Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. *Tetrahedron Lett.* **1971**, 4955.

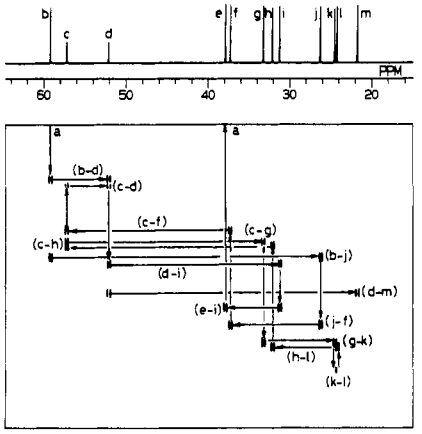
(4) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

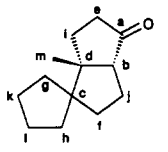
(5) See supplementary material in ref 1b.

(6) MM2 calculation showed that the ketone with 5*R** stereochemistry (cis–trans relationship between the three five-membered rings) is less stable by 22.5 kcal/mol than **16**.

(7) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106.

(8) The corresponding cis,trans ketone without the C(8)-methyl group rearranged via the new-type pathway to give cis,trans angularly fused ketone mainly.[1b]

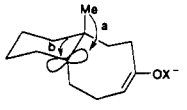




13

Figure 2. 2D ^{13}C-INADEQUATE spectrum (64–16 ppm) of **13**.

13 having a thermodynamically stable *cis*-bicyclo[3.3.0]-octane ring system (Scheme I). The difference of the migrating aptitude in **4** may be explained by a stereoelectronic effect as shown in **20**. Namely, the C(8)–C(9)



20

bond may be periplanar to the vacant p orbital while the methyl group may be not and the former bond migration may occur prior to conformational equilibration. In the corresponding cation **4** derived from **10**, migration of the methyl group is favored on the same grounds.

In this way, the novel rearrangement of **10** and **11** via the homoallylcarbinyl cation **4** gave the unique carbocyclic compounds efficiently. Further application of this rearrangement to the construction of other intriguing carbocyclic skeletons is in progress.

Experimental Section

Melting points were uncorrected. Instruments for the measurement of spectra and the techniques of chromatography were the same as were used in the previous work.[1b]

(1*R,4*S**,8*R**)- and (1*S**,4*R**,8*R**)-8-Methyltricyclo[6.4.0.0^{1,4}]dodecan-5-ones (10 and 11).** Irradiation of 2.50 g (15.2 mmol) of 6-methylbicyclo[4.4.0]dec-1(2)-en-3-one (**9**)[3] in 280 mL of CH_2Cl_2 for 3 h was performed as described previously[1b] to give three photoadducts in a ratio of 3:63:11, which were chromatographed on alumina (elution with ether/petroleum ether, 3:97) to give 0.42 g (14% yield) and 1.83 g (63% yield) of **10** and **11**, respectively. The minor component changed to **10** during chromatography.[4]

10: mp 91–95 °C; IR (KBr) 1700 cm^{-1}; MS *m/e* 192 (M$^+$, 52) 164 (95), 136 (58), 122 (100); ^{1}H NMR ($CDCl_3$) δ 2.7–1.0 (m, 17 H), 0.82 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.6 (s), 48.8 (d), 46.1 (s), 35.2 (t), 35.0 (t), 34.0 (t), 33.0 (s), 32.0 (t), 27.6 (t), 22.4 (t), 21.4 (t), 19.8 (q), 19.6 (t). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.13; H, 10.55.

11: mp 53–55 °C; IR (KBr) 1700 cm^{-1}; MS *m/e* 192 (M$^+$, 16), 164 (44), 112 (82), 97 (100); ^{1}H NMR ($CDCl_3$) δ 2.6-1.0 (m, 17 H), 0.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 215. 7 (s), 50.1 (d), 45.9 (s), 34.1 (t), 34.0 (t), 33.7 (s), 33.0 (t), 32.5 (t), 25.5 (t), 20.6 (t, 2 C), 18.7 (t), 17.1 (q). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.88; H, 10.12.

(1*S,5*S**,8*S**)-8-Methyltricyclo[6.4.0.0^{1,5}]dodecan-4-one (12).** A solution of 107 mg (0.56 mmol) of **10** and 149 mg (1.12 mmol) of $AlCl_3$ in 5 mL of CH_2Cl_2 was stirred at room temperature for 2 h. Water was added to the cooled mixture and the mixture was extracted with ether. The combined extracts were washed with $NaHCO_3$ solution and brine and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with ether/petroleum ether, 3:97) of the crude product gave, along with a small amount of unidentified product, 18 mg of recovered **10** and 63 mg (71% yield) of **12**: IR (neat) 1730 cm^{-1}; MS *m/e* 192 (M$^+$, 100), 163 (65), 135 (65); ^{1}H NMR ($CDCl_3$) δ 2.7–1.0 (m, 17 H), 0.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 222.9 (s), 54.8 (d), 53.9 (s), 43.9 (s), 38.8 (t), 37.1 (t), 36.0 (t), 30.8 (t), 30.6 (t), 25.1 (t), 22.6 (t), 22.1 (t), 19.0 (q). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.06; H, 10.53

(1*R,5*R**)-5-Methylbicyclo[3.3.0]octan-2-one-6-spiro-1′-cyclopentane (13).** Reaction of 100 mg (0.52 mmol) of **11** with 139 mg (1.04 mmol) of $AlCl_3$ for 1 h as described above gave along with a small amount of unidentified product 79 mg (79% yield) of an inseparable mixture of **12** and **13** whose ratio of 9:70 was determined by the ^{13}C NMR spectrum.

To a solution of 384 mg (2.00 mmol) of **11** in 20 mL of benzene was added 0.43 mL (ca. 8.0 mmol) of concentrated H_2SO_4 at room temperature. The mixture was stirred at that temperature for 24 h. Water was added to the cooled mixture. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phase was washed with $NaHCO_3$ solution and brine and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with ether/petroleum ether, 4:96) of the crude product gave 70 mg of recovered **11** and 242 mg (77% yield) of **13**: IR (neat) 1730 cm^{-1}; MS *m/e* 192 (M$^+$, 32), 97 (100); ^{1}H NMR ($CDCl_3$) δ 2.5–1.1 (m, 17 H), 1.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 223.4 (s), 59.3 (d), 57.2 (s), 52.2 (s), 37.8 (t), 37.4 (t), 33.3 (t), 32.1 (t), 31.2 (t), 26.2 (t), 24.5 (t), 24.2 (t), 21.7 (q). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.22; H, 10.56.

(1*S,4*R**,8*R**)-8-Methyltricyclo[6.4.0.0^{1,4}]dodecan-5-yl *m*-Bromobenzoate (14).** Reduction of 167 mg (0.87 mmol) of **11** with 17 mg (0.43 mmol) of $LiAlH_4$ was performed as described previously[1b] to give 141 mg (84% yield) of a mixture (2:98) of two alcohols after flash chromatography (elution with ether/petroleum ether, 25:75): IR (KBr) 3250, 1240 cm^{-1}.

Esterification of 69 mg (0.38 mmol) of the above alcohols with *m*-bromobenzoyl chloride was done as described previously[1b] to give 121 mg (90% yield) of **14** after flash chromatography (elution with ether/petroleum ether, 4:96) followed by recrystallization from hexane: mp 95–97 °C; IR (KBr) 1710, 1570, 1290, 1265, 1125, 995, 980, 965, 890, 754, 715 cm^{-1}; MS *m/e* 378 (M$^+$ + 2, trace), 376 (M$^+$, trace), 185 (64), 183 (65), 176 (100), 161 (51), 148 (90), 133 (66), 94 (53); ^{1}H NMR ($CDCl_3$) δ 8.16 (dd, *J* = 2.0, 2.0 Hz, 1 H), 7.96 (ddd, *J* = 7.8, 2.0, 1.0 Hz, 1 H), 7.66 (ddd, *J* = 7.8, 2.0, 1.0 Hz, 1 H), 7.31 (dd, *J* = 7.8, 7.8 Hz, 1 H), 5.27 (ddd, *J* = 9.8, 5.9, 5.9 Hz, 1 H), 2.19–2.09 (m, 2 H), 2.05–1.97 (m, 1 H), 1.93–1.87 (m, 1 H), 1.84–1.74 (m, 1 H), 1.73–1.43 (m, 8 H), 1.44–1.36 (m, 1 H), 1.26 (ddd, *J* = 13.7, 4.4, 4.4 Hz, 1 H), 1.17–1.06 (m, 2 H), 1.00 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.9 (s), 135.9 (d), 132.9 (s), 132.6 (d), 129.8 (d), 128.2 (d), 122.4 (s), 79.4 (d), 46.7 (s), 41.6 (d), 34.5 (t), 33.7 (t), 32.9 (s), 30.3 (t), 25.6 (t), 24.7 (t), 24.0 (t), 21.2 (t), 20.7 (t), 19.3 (q). Anal. Calcd for $C_{20}H_{25}O_2Br$: C, 63.66; H, 6.68; Br, 21.18. Found: C, 63.81; H, 6.69; Br, 21.11.

(1*S,5*S**,8*S**)-5-Methyltricyclo[6.3.0.0^{1,5}]undec-2-en-4-one (16).** To a solution of LDA prepared from 2.15 mL (15.3 mmol) of diisopropylamine and 10.2 mL (15.3 mmol) of BuLi in hexane in 80 mL of dry THF was added dropwise a solution of 2.00 g (12.3 mmol) of (1*S**,5*S**,8*S**)-tricyclo[6.3.0.0^{1,5}]undec-2-en-4-one (**15**)[5] and 2.15 mL (12.3 mmol) of hexamethylphosphoramide in 50 mL of dry THF at −78 °C during 25 min under N_2. The solution was stirred for 30 min at −78 °C and then 7.69 mL (123 mmol) of methyl iodide was added. The solution was stirred at −78 °C for 3 h and poured into NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phase was washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with ether/petroleum ether, 1:9) of the crude product gave 2.10 g (97% yield) of **16**: mp 42–42.5 °C; IR (KBr) 1700, 1580 cm^{-1}; MS *m/e* 176 (M$^+$, 100), 161 (80), 148 (51); ^{1}H

NMR (CCl_4) δ 7.32 (d, J = 6.0 Hz, 1 H), 5.90 (d, J = 6.0 Hz, 1 H), 2.4-1.1 (m, 11 H), 1.00 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.0 (s), 170.9 (d), 129.2 (d), 66.5 (s), 57.4 (s), 49.4 (d), 36.4 (t), 33.2 (t), 32.2 (t), 29.0 (t), 27.3 (t), 19.3 (q). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.83; H, 9.25.

(1*R,5*S**,8*S**)-5-Methyltricyclo[6.3.0.0^{1,5}]undecan-4-one (17).** A mixture of 1.05 g (5.95 mmol) of **16** and a catalytic amount of 10% palladized carbon in 90 mL of ethyl acetate was stirred at room temperature for 2 h under 1 atm of H_2. After filtration, the filtrate was concentrated and flash chromatography (elution with ether/petroleum ether, 3:97) of the crude product gave 0.93 g (88% yield) of **17**: mp 58-60 °C; IR (KBr) 1730 cm^{-1}; MS m/e 178 (M^+, 86), 122 (82), 121 (100), 107 (70); ^1H NMR (CCl_4) δ 2.4-1.1 (m, 15 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 226.6 (s), 60.6 (s), 58.8 (s), 51.3 (d), 37.8 (t), 37.3 (t), 36.1 (t), 35.9 (t), 32.7 (t), 31.8 (t), 27.1 (t), 17.0 (q). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.56; H, 10.23.

(1*R,5*R**,8*S**)-8-Methyltricyclo[6.4.0.0^{1,5}]dodecan-9-one (18).** To a solution of LDA (6.50 mmol) in 5 mL of dry THF was added dropwise a solution of 930 mg (5.22 mmol) of **17** in 6 mL of dry THF at -78 °C during 6 min under N_2. The solution was stirred at -78 °C for 1 h and 1.33 mL (10.4 mmol) of trimethylsilyl chloride was added. The mixture was warmed to room temperature and stirred at that temperature for 2 h. The mixture was filtered and the filtered solid was washed with petroleum ether. The combined filtrate was concentrated to give the residue, which was diluted with petroleum ether. The mixture was filtered again. The filtration was repeated until the filtrate became a clear solution to give the crude silyl enol ether: IR (neat) 3050, 1645, 1255, 845 cm^{-1}.

To a solution of the above enol ether in 15 mL of hexane was added 1.20 mL (11.7 mmol) of diethylzinc at room temperature under N_2. To the solution was added dropwise 1.26 mL (15.7 mmol) at diiodomethane during 30 min. The mixture was stirred at room temperature for 2 h and cold NH_4Cl solution was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phase was washed with $NaHCO_3$ solution and brine and dried ($MgSO_4$). Evaporation of the solvent gave the crude siloxycyclopropane: IR (neat) 3030, 1245, 830 cm^{-1}.

To a solution of 2.55 g (15.7 mmol) of anhydrous $FeCl_3$ in 11 mL of dimethylformamide was added dropwise a solution of the above cyclopropane and 0.46 mL (5.74 mmol) of pyridine in 11 mL of the same solvent at 0 °C during 30 min under N_2. The solution was stirred at 0 °C for 10 min and then at room temperature for 3 h. Cold 5% HCl was added and then the mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the crude ring-expanded chloride: IR (neat) 1700 cm^{-1}.

A mixture of the above chloride and 4.28 g (52.2 mmol) of sodium acetate in 50 mL of MeOH was stirred at reflux for 7 h. After evaporation of the solvent, water was added. The mixture was extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by the column chromatography (elution with ether/petroleum ether, 2:98) of the crude product gave 107 mg of recovered **17** and 225 mg (26% yield from **17**) of the enone: IR (neat) 1670 cm^{-1}: MS m/e 190 (M^+, 13), 122 (100), 107 (59): ^1H NMR ($CDCl_3$) δ 6.9-6.6 (m, 1 H), 5.95 (d, J = 9.8 Hz, 1 H), 2.4-1.1 (m, 13 H), 1.05 (s, 3 H).

Hydrogenation of 209 mg (1.10 mmol) of the above enone for 1 h as described above gave 195 mg (93% yield) of **18** after flash chromatography (elution with ether/petroleum ether, 3:97): IR (neat) 1700 cm^{-1}; MS m/e 192 (M^+, 100), 124 (69), 121 (94), 108 (52), 93 (54); ^1H NMR ($CDCl_3$) δ 2.7-1.1 (m, 17 H), 1.08 (s, 3 H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.87; H, 10.53.

(1*S,5*S**,8*S**)-8-Methyltricyclo[6.4.0.0^{1,5}]dodecane (19). Method A. Wolff-Kishner Reduction of 12.** A solution of 220 mg (1.15 mmol) of **12**, 450 mg (8.02 mmol) of KOH, and 0.70 mL (11.5 mmol) of 80% hydrazine hydrate in 5 mL of diethylene glycol was refluxed at ca. 150 °C for 3 h. Excess hydrazine and water were distilled off and the solution was heated at 210 °C for 4 h. The cooled solution was neutralized with 5% HCl and the mixture was extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with petroleum ether) of the crude product gave 133 mg (65% yield) of **19**: IR (CCl_4) 2930, 2850, 1450, 1370 cm^{-1}; MS m/e 178 (M^+, 23), 163 (45), 135 (100); ^1H NMR ($CDCl_3$) δ 2.2-1.0 (m, 19 H), 0.95 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 56.5 (s), 44.4 (d), 43.4 (s), 39.9 (t), 36.9 (t), 36.7 (t), 34.0 (t), 32.4 (t), 30.1 (t), 24.5 (t), 23.4 (t), 22.5 (t), 21.4 (q). Anal. Calcd for $C_{13}H_{22}$: C, 87.56: H, 12.44. Found: C, 87.65; H, 12.52.

Method B. Wolff-Kishner Reduction of 18. Reduction of 177 mg (0.92 mmol) of **18** as described above gave 108 mg (66% yield) of a hydrocarbon whose ^{13}C NMR spectrum is identical with that of **19** obtained by method A.

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Supplementary Material Available: Details of X-ray crystallographic analysis of **14** and Tables I-III listing the bond lengths, bond angles, atomic coordinates, and anisotropic parameters of **14** (8 pages). Ordering information is given on any current masthead page.

Two Dimers Derived from the 2,4,6-Tri-*tert*-butylphenyl Radical, Formed during Reactions of the Aryllithium or the Grignard Reagent with Carbonyl Compounds

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The 2,4,6-tri-*tert*-butylphenyl radical **1**• was generated from 1-bromo-2,4,6-tri-*tert*-butylbenzene (**1**-Br) with Me_3Sn•, and its isomeric radical 3,5-di-*tert*-butylneophyl **2**• from photolysis of 1,3,5-tri-*tert*-butylbenzene (**1**-H) with *t*-BuOOBu-*t*, and their ESR spectra were measured.[1] On raising the temperature in the **1**•-forming reaction, **2**• is observed, and from the kinetics of the decay of both species, eq 1 was suggested, where $(2)_2$ is a dimer that was

$$1^\bullet \xrightarrow{\text{isom}} 2^\bullet \rightarrow (2)_2 \qquad (1)$$

not isolated or identified. For **1**• at 25 °C log ($\tau_{1/2}$/s) = -2.2.[1a,c] On thermal decomposition of *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate, the ESR spectrum of **2**• was also observed,[2] and only methyl 2,4,6-tri-*tert*-butylbenzoate was identified after CH_2N_2 treatment. In spite of the known neopentyl radical rearrangement,[3] the rearranged radical **3**• was not observed under these conditions.[4]

(1) (a) Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 3011. (b) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *Ibid.* **1976**, *98*, 6803. (c) For a review of persistent carbon stable radicals, see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *109*, 13.

(2) Icli, S.; Kandil, A. K.; Thankachan, C.; Tidwell, T. T. *Can. J. Chem.* **1975**, *53*, 979.

(3) Hamilton, E. J., Jr.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795.

(4) It was quoted in ref 1b that **3**• is formed from **2**•, according to ref 3 and to Maillard, B.; Ingold, K. U. (*J. Am. Chem. Soc.* **1976**, *98*, 1224), but only rearrangements of related radicals were reported.

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