spectrometer. Optical rotations were obtained on a JASCO DIP-360 polarimeter and CD spectra on a JASCO J-40A spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 or AM-500 spectrometer. The 7.27 ppm resonance of residual $CHCl_3$ and 76.9 ppm of $CDCl_3$ were used as internal references for ^1H and ^{13}C NMR, respectively. ^1H Selective probehead for inverse experiments (400 MHz, Bruker Co.) was used in HMBC measurements. Mass spectra were obtained on a Shimadzu GC-MS QP-1000A operating at 70 eV (for LREI) or a JEOL HX-100 spectrometer (for FAB and HREI).

Collection, Extraction, and Separation. *P. melanos*, a green sponge, was collected at Motobu Peninsula (-2 to -3 m) of Okinawa Island in June 1986 by using SCUBA and kept frozen until used. The sponge (900 g, wet weight) was crushed and extracted with methanol/toluene (3:1, 1500 mL × 2). The extract was partitioned between toluene (500 mL × 2) and 1 M NaCl (1500 mL). The aqueous layer was extracted with chloroform (500 mL × 2). After evaporation of the solvent under reduced pressure, the chloroform-soluble material (1.49 g) was chromatographed on a silica gel column (Wako gel C-300, Wako Chemicals, 30 × 600 mm) with MeOH/$CHCl_3$ (2:98 to 20:80) to give three fractions of a (780–990 mL), b (1210–1900 mL), and c (2110–2660 mL). The less polar fraction a was further purified on a Sephadex LH-20 column (Pharmacia Fine Chemicals, 30 × 900 mm) with $CHCl_3$/MeOH (1:1) followed by a silica gel column (Wako gel C-300, 15 × 600 mm) with petroleum ether/$CHCl_3$/MeOH (20:5:1) to afford prianosins A (**1**, 180 mg) and B (**2**, 14 mg). Each of polar fractions (b and c) was evaporated under reduced pressure and passed through a Sephadex LH-20 column (30 × 900 mm) with $CHCl_3$/MeOH (1:1) to give prianosins C (**3**, 60 mg) and D (**4**, 71 mg), respectively.

Prianosin A[4] (1): CD (MeOH) λ_{ext} 360 ($\Delta\epsilon$ -3.7), 309 (+2.4), 271 (+2.0), and 233 (-7.1) nm.

Prianosin B (2): a red crystal; mp 250–251 °C dec; $[\alpha]^{30}_D$ +360° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} 228 (ϵ 17 800), 263 (15 000), 410 (sh), and 430 (11 200) nm; IR (KBr) ν_{max} 3350, 1670, 1640, 1600, 1460, 1300, and 1210 cm^{-1}; CD (MeOH) λ_{ext} 360 ($\Delta\epsilon$ -2.7), 265 (+3.6), and 233 (-8.8) nm; ^1H NMR ($CDCl_3$) δ 2.88 (m, H-7), 2.95 (dd, *J* = 16.9 and 6.7 Hz, H-4), 3.01 (dd, *J* = 16.9 and 12.5 Hz, H-4), 4.79 (dd, *J* = 12.5 and 6.7 Hz, H-5), 5.47 (m, H-8), 7.51 (d, *J* = 5.9 Hz, H-16), 7.78 (s, H-14), 7.96 (s, H-1), and 8.46 (d, *J* = 5.9 Hz, H-17); ^{13}C NMR ($CDCl_3$/CD_3OD, 4:1) δ 40.3 (t, C-7), 45.8 (t, C-4), 51.1 (s, C-6), 56.6 (d, C-5), 61.8 (d, C-8), 113.8 (d, C-16), 117.4 (s), 119.0 (s), 120.2 (s, C-2), 125.3 (d, C-14), 128.4 (s, 2 × C), 142.9 (d, C-17), 143.7 (s), 149.1 (s), 156.8 (d, C-1), 170.5 (s, C-11), and 189.2 (s, C-3); FABMS (glycerol), *m/z* 414 (M^+ + H) and 416 (M^+ + 2 + H).

Prianosin C (3): a green solid; mp >300 °C; $[\alpha]^{22}_D$ +358° (*c* 0.01, MeOH); UV (MeOH) λ_{max} 231 (ϵ 12 300), 263 (3900), 292 (2100), and 370 (1280) nm; IR (KBr) ν_{max} 3400–3100, 2945, 1650, 1630, 1600, 1540, 1500, 1430, 1320, 1220, 1180, 1130, 1090, 1040, 990, 845, 800, and 740 cm^{-1}; CD (MeOH) λ_{ext} 352 ($\Delta\epsilon$ +41.1), 308 (-17.3), and 258 (-43.3) nm; FABMS (glycerol), *m/z* 354 (M^+ + H); EIMS, *m/z* 353 (M^+), 336 (M^+ - HO), and 266 (M^+ - C_3H_3OS).

Prianosin C Acetate (5): To 25.0 mg of prianosin C (**3**) were added pyridine (2 mL) and acetic anhydride (2 mL), standing at room temperature overnight. After evaporation of organic solvents under reduced pressure, the residue was chromatographed on a short silica gel column (Wako gel C-300, 10 × 100 mm) with $CHCl_3$/MeOH (99:1) to give the triacetate (**5**, 4.6 mg): a yellow crystal; mp 200–201 °C dec; $[\alpha]^{23}_D$ +384° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} 245 (ϵ 21 000), 279 (17 000), 370 (3200), and 419 (2800) nm; IR (KBr) ν_{max} 3500–3200, 3090, 2925, 2850, 1740, 1650, 1570, 1370, 1310, 1240, 1180, 1150, 1050, 1030, 990, 900, 845, 800, and 740 cm^{-1}; FABMS (glycerol), *m/z* 480 (M^+ + H); EIMS, *m/z* 479 (M^+), 437 (M^+ - 2Ac - H), 352 (M^+ - 3Ac), 308 (M^+ - 2Ac - C_3H_2OS), and 266 (308 - Ac); ^1H NMR ($CDCl_3$) δ 2.24 (s, Me), 2.32 (dd, *J* = 11.7 and 4.0 Hz, H-7), 2.34 (s, Me), 2.44 (d, *J* = 11.7 Hz, H-7), 2.53 (d, *J* = 12.2 Hz, H-1), 2.53 (m, H-17), 2.63 (s, Me), 2.93 (m, *J* = 15.7, 2.0, and 1.5 Hz, H-16), 3.04 (m, *J* = 15.7, 4.8, and 2.0 Hz, H-16), 3.45 (d, *J* = 12.2 Hz, H-1), 3.83 (ddd, *J* = 12.5, 4.8, and 2.0 Hz, H-17), 5.98 (s, H-4), 6.88 (d, *J* = 1.5 Hz, H-14), 7.03 (d, *J* = 4.0 Hz, H-8), and 10.18 (s, 11-OH); ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 22.2 (t, C-16), 23.4 (q), 23.5 (q), 32.7 (t, C-1), 42.7 (s and t, C-6 and C-7), 47.9 (t, C-17), 64.7 (d, C-8), 88.6 (s, C-2), 111.8 (s, C-20), 115.0 (d, C-5), 117.6 (d, C-14), 118.8 (s, C-15), 119.5 (s, C-21), 120.4 (s, C-10). 123.9 (s, C-12), 126.6 (s, C-19), 133.6 (s, C-11), 169.4 (s, 2-OCO), 171.0 (s, 9-NCO), 173.1 (s, 13-NCO), 174.8 (s, C-5), and 181.0 (s, C-3).

Prianosin D (4): a green solid; mp >300 °C; $[\alpha]^{26}_D$ +344° (*c* 0.01, MeOH); UV (MeOH) λ_{max} 250 (ϵ 18 100), 284 (11 100), 325 (6600), and 392 (6950) nm; IR (KBr) ν_{max} 3400–3100, 2945, 1660, 1630, 1600, 1540, 1500, 1430, 1320, 1300, 1220, 1180, 1135, 1110, 980, and 900 cm^{-1}; CD (MeOH) λ_{ext} 360 ($\Delta\epsilon$ +45.8), 304 (-11.5), and 255 (-34.4) nm; FABMS (glycerol), *m/z* 338 (M^+ + H); EIMS, *m/z* 337 (M^+), 304 (M^+ - HS), and 249 (M^+ - C_3H_4OS).

Prianosin D Acetate (6). To 25.0 mg of prianosin D (**4**) were added pyridine (2 mL) and acetic anhydide (2 mL). The mixture stood overnight at room temperature. The same workup as described for **5** yielded the diacetate (**6**, 14.6 mg): a yellow crystal; mp 256–259 °C dec; $[\alpha]^{25}_D$ +341° (*c* 0.03, $CHCl_3$); UV (MeOH) λ_{max} 247 (ϵ 19 700), 280 (17 600), and 350 (4400) nm; IR (KBr) ν_{max} 3500–3200, 3125, 2925, 2850, 1660, 1640, 1615, 1570, 1480, 1420, 1360, 1300, 1270, 1140, 990, and 740 cm^{-1}; ^1H and ^{13}C NMR (Table I); FABMS (glycerol), *m/z* 422 (M^+ + H); EIMS, *m/z* 421 (M^+), 379 (M^+ - Ac), 346 (M^+ - Ac - HS), 336 (M^+ - 2Ac - H), 292 (M^+ - Ac - C_3H_3OS), and 250 (292 - Ac); HREIMS found *m/z* 421.1094, calcd for $C_{22}H_{19}N_3O_4S$ 421.1092 (M).

Biological Assay. The extravesicular Ca^{2+} concentration in sarcoplasmic reticulum was monitored with a Ca^{2+} electrode prepared by the method of Tsien and Rink with modifications.[20]

Antitumor activity was determined by using murine lymphomas L1210, L5178Y, and human epidermoid carcinoma KB cells. Roswell Park Memorial Institute Medium 1640 supplemented with 10% heat-inactivated fetal bovine serum and 50 μg/mL of kanamycin was used as the cell cultured medium. Tumor cells (5×10^4 cells/mL) were cultured in a CO_2 gas incubator at 37 °C for 48 h in 1 mL of medium containing various concentrations of test compound. Their viability, estimated by use of a variation of a colorimetric [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] (MTT) assay,[21] was compared to that of control cells incubated in the identical medium without the compound. The antitumor activity evaluated as IC_{50} (the concentration in μg/mL required for 50% inhibition of cell growth). The IC_{50} value was obtained by plotting the logarithm of concentration of test compound vs the growth rate (percentage of control) of the treated cells.

Acknowledgment. We thank Dr. T. Hoshino of Mukaishima Marine Biological Station, Hiroshima University, for identification of the sponge, Z. Nagahama for help with collections, and M. Hamashima for technical assistance. This study was supported in part by Grant-in-Aid (62010049) for Cancer Research from Ministry of Education, Science, and Culture, Japan.

Supplementary Material Available: Two figures containing the HOHAHA spectrum of prianosin D acetate (**6**) and the ^1H–^{13}C COSY spectrum of prianosin D acetate (**6**) (3 pages). Ordering information is given on any current masthead page.

(21) Carmichael, J.; DeGraff, W. G.; Gazdar, A. F.; Minna, J. D.; Mitchell, J. B. *Cancer Res.* **1987**, *47*, 936–942.

Thermal Isomerizations of 2-Methylenebicyclo[2.1.0]pentane

Gerald D. Andrews and John E. Baldwin*,[1]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

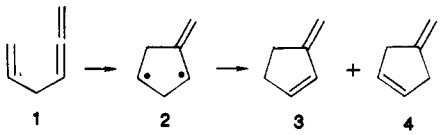
Received April 8, 1988

It has been known since 1966 that 1,2,5-hexatriene (**1**) isomerizes at 340–385 °C in a flow system to both 3- and 4-methylenecyclopentene (**3** and **4**), presumably by way

(1) Present address: Department of Chemistry, Syracuse University, Syracuse, NY 13244.

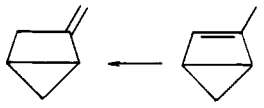
0022-3263/88/1953-4624$01.50/0

of the diradical intermediate 4-methylenecyclopentane-1,3-diyl (2).[2]



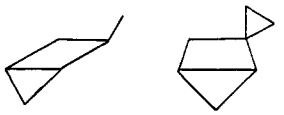
1 2 3 4

2-Methylenebicyclo[2.1.0]pentane (5) was not found in the product mixtures, a fact rationalized on thermochemical grounds.[2] Whether 5 may serve as an alternative precursor to diradical 2 was not probed experimentally by Huntsman and co-workers[2], but Brinker and Erdle[3] have just shown that 1,3,3-trimethyl-2-methylenebicyclo-[2.1.0]pentane exhibits thermal chemistry consistent with its isomerization to the 3,5,5-trimethyl-4-methylenecyclopentane-1,3-diyl diradical. Their publication[3] prompts the present report on the preparation and thermal chemistry of the parent 2-methylenebicyclo[2.1.0]pentane (5).



5 6

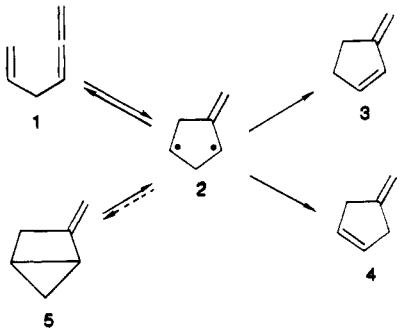
Base-catalyzed isomerization[4] of 2-methylbicyclo-[2.1.0]pentene (6) provides a convenient source of hydrocarbon 5. In 1 M sodium methylsulfinylmethide in dimethyl sulfoxide at room temperature, the reaction 6 → 5 goes to completion with a half-life of about 20 min. Mass spectrometry and ^{1}H NMR spectroscopy confirmed formula C_6H_8 and structural assignment 5. Reduction of 5 with diimide generated from potassium azodicarboxylate and acetic acid gave with high diastereofacial selectivity *exo*-2-methylbicyclo[2.1.0]pentane (7);[5] cyclopropanation of 5 with benzylmecurioiodomethane[6] or with diazomethane/cupric chloride[7] afforded bicyclo[2.1.0]pentane-2-spirocyclopropane (8).



7 8

At 253 °C in a flow system, 2-methylenebicyclo[2.1.0]-pentane gave three major products that proved to be the known isomers[2,8] 1 (34%), 3 (32%), and 4 (23%). The observed 3:4 product ratio (32:23, or 1.4:1) compares closely with the reported 3:4 ratio from isomerization of 1 at 340–385 °C (1.3:1).[2] The activation energy for first-order conversion of 5 to products, estimated by a gas-chromatographic method,[9] was 36 kcal/mol.

Scheme I



These results may be summarized as shown in Scheme I: the diradical 2 may be formed from either 1 or 5 and may give 1 as well as 3 and 4. Whether 5 and 2 equilibrate faster than isomers 1, 3, and 4 are formed remains to be seen.

Experimental Section

Proton NMR spectra were obtained on a Varian Associates XL-100-FT spectrometer; mass spectra were run on a CEC 110-21 B instrument by Dr. Susan Rottschaefer. Perkin-Elmer Model F-11 and Varian Aerograph Model A-90-P3 and 1520 gas chromatographs were used for analytical and preparative separations.

2-Methylenebicyclo[2.1.0]pentane (5). A 500-mL photolysis vessel equipped with a nitrogen inlet at the bottom, a nitrogen outlet, and a water-cooled quartz photolysis well with a 450-W Hanovia medium-pressure lamp was charged with 300 mL of decalin and 10 mL of a mixture of 1- and 2-methylcyclopentadiene. The photolysis vessel was cooled externally with an ice–salt bath during the entire photolysis. A very slow stream of nitrogen was bubbled through the solution as the lamp was started and during the next hour, then a 100-mL dry ice–acetone cooled trap with the inlet submerged in about 20 mL of decalin was connected to the outlet of the photolysis vessel. The nitrogen flow was increased to about 200 mL/min during the next 5 h of photolysis. Meanwhile, a solution of NaH (10 g of 57% oil dispersion) in 200 mL of DMSO was prepared. The contents of the trap were added to the DMSO solution (two layers) and allowed to stir vigorously for 1 h at room temperature. The volatile components were then vacuum transferred into a liquid nitrogen cooled trap at 10–1 mm pressure with a nitrogen bleed through the DMSO mixture. About 0.9 mL of colorless liquid was obtained and analyzed on a 5 m × 6 mm 20% TCEP on 60/80-mesh Chromosorb P column with column, injection port, and detector at room temperature and a 100 mL/min flow rate. Under these conditions the retention times of 1-methylbicyclopentene, 2-methylbicyclopentene, and 2-methylenebicyclopentane were 5.4, 10.4, and 20 min, respectively. The major products were 1-methylbicyclopentene and 2-methylenebicyclopentane: collection of these by preparative GLC with liquid nitrogen cooled collectors on the above column gave about 300 mg each of these two hydrocarbons. 2-Methylenebicyclo[2.1.0]pentane (5) had mass spectral M^+ at m/e 80.063 (calcd for C_6H_8, 80.062) and ^{1}H NMR absorptions in $CDCl_3$ at δ 4.68 (C6-*Z*H), 4.44 (C6-*E*H), 2.59 (C3-*exo*-H), 2.22 (C1H), ~2 (2H, C4H and C3-*endo*-H), 1.05 (C5-*exo*-H), and 0.84 (C5-*endo*-H).

The base-catalyzed isomerization of 2-methylbicyclo[2.1.0]-pent-2-ene to 2-methylenebicyclo[2.1.0]pentane was followed directly in a separate experiment: small samples of a stirred solution of 10 mg of GLC-purified 6 in degassed 1 M sodium methylsulfinylmethide in DMSO at room temperature were removed periodically, dripped over ice, and extracted with a comparable volume of pentane. Analysis of the pentane solutions obtained by GLC on the TCEP column at room temperature gave relative concentrations of 5 and 6 as a function of time appropriate to a pseudo-first-order isomerization having $k = 6 \times 10^{-4}$ s^{-1} or $t_{1/2} = \sim 20$ min.

(2) Huntsman, W. D.; DeBoer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846–5850. See also: Huntsman, W. D. *Intra-Sci. Chem. Rep.* **1972**, *6*, 151–159. Dalacker, V.; Hopf, H. *Tetrahedron Lett.* **1974**, 15–18.

(3) Brinker, U. H.; Erdle, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1260–1262.

(4) Compare: Hubert, A. J.; Reimlinger, H. *Synthesis* **1969**, 97–112. Koster, R.; Arora, S.; Binger, P. *Synthesis* **1971**, 322–323.

(5) Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250–3253. Harmony, M. D.; Wang, C. S.; Wiberg, K. B.; Bishop, K. C., III. *J. Chem. Phys.* **1975**, *63*, 3312–3316.

(6) Schefford, R.; Michel, U. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 231–232. Baldwin, J. E.; Andrews, G. D. *J. Org. Chem.* **1973**, *38*, 1063.

(7) Compare: Baldwin, J. E.; Ollerenshaw, J. *Tetrahedron Lett.* **1972**, 3757–3760. Van den Enden, L.; Geise, H. J.; Figeys, H. P.; Geerlings, P.; Van Alsenoy, C. *J. Mol. Struct.* **1976**, *33*, 69–77.

(8) Peiffer, G. *Bull. Soc. Chim. Fr.* **1962**, 776–777. Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749–4751. Viola, A.; Madhavan, S.; Proberb, R. J. *J. Org. Chem.* **1974**, *39*, 3154–3156.

(9) Schmiegel, W. W.; Litt, F. A.; Cowan, D. O. *J. Org. Chem.* **1968**, *33*, 3334–3335.

(10) Compare: Andrist, A. H.; Baldwin, J. E.; Pinschmidt, R. K., Jr. *Org. Synth.* **1976**, *55*, 15–19. Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818–1829.

Table I. Isomerization of 5 in Constant-Time Flow Reactor

T (°C)	[5]	ln ln (1/[5])
223.1	0.689	-0.987
226.9	0.518	-0.419
232.0	0.385	-0.047
232.4	0.386	-0.049
240.0	0.241	+0.353
241.9	0.218	+0.421

Reduction of 2-Methylenebicyclo[2.1.0]pentane (5) with Diimide. To a solution of about 100 mg of **5** in 3 mL of ether at room temperature was added 500 mg of potassium azodicarboxylate followed by dropwise addition by syringe of 300 mg of acetic acid. Analysis by GLC showed partial conversion of starting material; the reaction mixture was treated again with potassium azodicarboxylate followed by acetic acid. Product was isolated by preparative GLC and identified by ^{1}H NMR spectroscopy as the known[5] exo isomer of 2-methylbicyclo[2.1.0]-pentane (**7**).

Bicyclo[2.1.0]pentane-2-spirocyclopropane (8). Benzylmecurioiodomethane[6] (1.2 g) and 100 mg of olefin **5** were heated in a sealed, degassed tube at 80 °C for 4 h. Volatile compounds from the sealed-tube reaction were isolated by vacuum transfer and purified by GLC: one major product was apparent, and all starting material had been consumed. The product had M^+ at m/e 94.078 (calcd for C_7H_{10}, 94.078) and ^{1}H NMR absorptions appearing as complex multiplets centered at δ 2.18 (1 H), 1.68 (1 H), 1.46 (2 H), 0.76 (2 H), 0.54 (2 H), and 0.20 (2 H).

Alternatively, treatment of **5** in ether with ethereal diazomethane[7] in the presence of cupric chloride afforded the spirocyclopropane product **8** in approximately 10% yield.

Thermal Isomerizations of 2-Methylenebicyclo[2.1.0]-pentane (5). Gas-phase pyrolysis of four 10-μL injections of GLC-purified **5** at 253 °C using a 50-μL reaction chamber[11] and dry nitrogen as carrier gas at a flow rate of 44 mL/min gave a reaction mixture that was collected in a liquid nitrogen cooled trap and shown by GLC analysis to contain four major components (together, more than 95% of all integrated GC peak intensities) with relative retention times of 1, 1.15, 1.29, and 1.73. They were isolated by preparative GLC and found to be, respectively, 4-methylenecyclopentene (**4**; 23%), 1,2,5-hexatriene (**1**; 34%), starting material (**5**; 11%), and 3-methylenecyclopentene (**3**; 32%). The isomeric products were each identified by mass spectrometry (M^+, m/e 80) and through their characteristic and known[2,8] infrared and ^{1}H NMR spectra.

Pyrolysis of **5** in the injection port of the Perkin-Elmer Model F-11 gas chromatograph as a function of injection block temperature at a constant carrier gas flow rate between 223 and 242 °C gave data on extent of isomerization as summarized in Table I. A plot[9] of ln ln (1/[**5**]) against $T(K)^{-1}$ gave 36 kcal/mol as an estimate for E_a.

Acknowledgment. We thank the National Science Foundation for financial support of our work on hydrocarbon thermal rearrangements.

(11) Cooke, R. S.; Andrews, U. H. *J. Org. Chem.* **1973**, *38*, 2725-2727; *J. Am. Chem. Soc.* **1974**, *96*, 2974-2980.

Synthesis of Hexamethylglutaric Acid: An Approach to Compounds with Adjacent Quaternary Carbon Centers

Janusz Baran and Herbert Mayr*

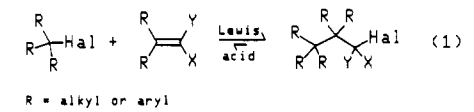
Institut für Chemie, Medizinische Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

Received February 9, 1988

The construction of quaternary carbon centers often requires a special methodology since many of the transformations that are frequently employed for carbon–carbon bond formations are not applicable to the efficient creation of quaternary carbon centers.[1] Reactions of tertiary alkyl halides with carbon nucleophiles, for example, usually result in the formation of elimination instead of substitution products.

In several instances, quaternary carbon centers have been generated by reactions proceeding via tertiary carbenium ions. Examples are the *tert*-alkylations of carbonyl compounds,[2] reactions of *tert*-alkyl halides with alkylaluminium[3a] or alkyltitanium compounds,[3b] geminal dimethylations of ketones,[3c] carbocationic cyclizations,[4] and Lewis acid catalyzed additions of alkyl and allyl halides toward alkenes.[5]

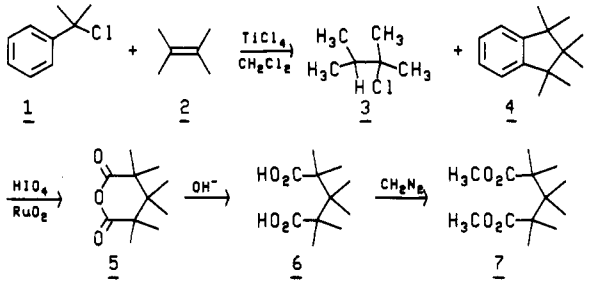
Problems were encountered, however, in attempts to employ the latter process for the generation of two or more adjacent quaternary carbons. In these cases, the free energy gained from the formation of a new σ-bond is usually not sufficient to compensate for the increase of steric strain, and equilibrium (1) is not in favor of the addition products.



(1)

We report now a simple strategy for the generation of adjacent quaternary carbons in acyclic compounds. This method prevents the reverse reaction (1) by initially fixing the two fragments in a ring, which is then opened at a position remote from the quaternary centers.

When $TiCl_4$ (57 mmol) was added to a solution of 2-chloro-2-phenylpropane (cumyl chloride) **1** (0.53 mol) and tetramethylethylene (**2**) (1.3 mol) in dichloromethane at −75 °C, the hexamethylindan (**4**) was formed in 72% yield.[6] Hydrogen chloride liberated in this process was trapped by excess **2** to give 2-chloro-2,3-dimethylbutane (**3**). In analogy with the corresponding allyl cation additions to alkenes,[5b,7] the cumulation of the alkyl groups accelerates the cyclization of the acylic intermediates (geminal dialkyl effect[8]), and precursors of **4** are not detectable.



1 2 3 4 5 6 7

Oxidation of **4** with $NaIO_4/RuO_2$ in $CCl_4/CH_3CO_2H/H_2O$ gave 64% of the anhydride **5**, which was hydrolyzed

(1) Martin, S. F. *Tetrahedron* **1980**, *36*, 419.
(2) Reetz, M. T. *Angew. Chem.* **1982**, *94*, 97; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 96.
(3) (a) Kennedy, J. P.; Desai, N. V.; Sivaram, S. *J. Am. Chem. Soc.* **1973**, *95*, 6386. (b) Reetz, M. T.; Westermann, J.; Steinbach, R. *Angew. Chem.* **1980**, *92*, 933; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 901. (c) Reetz, M. T.; Westermann, J.; Kyung, S.-H. *Chem. Ber.* **1985**, *118*, 1050.
(4) Reviews: (a) Johnson, W. S. *Angew. Chem.* **1976**, *88*, 33; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9. (b) Sutherland, J. K. *Chem. Soc. Rev.* **1980**, *9*, 265. (c) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, 1984; Vol. 3B, pp 341.
(5) (a) Mayr, H.; Striepe, W. *J. Org. Chem.* **1983**, *48*, 1159. (b) Mayr, H.; Klein, H.; Kolberg, G. *Chem. Ber.* **1984**, *117*, 2555.
(6) Henkes, E.; Halbritter, K.; Mayr, H.; Striepe, W.; Pock, R. Verfahren zur Herstellung von Indanen. Europ. Patent Application 87110537.5.
(7) Klein, H.; Mayr, H. *Angew. Chem.* **1981**, *93*, 1069; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027.
(8) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1, pp 58.

0022-3263/88/1953-4626$01.50/0