

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 ¹H NMR spectroscopy as the known⁵ exo isomer of 2-methylbicyclo[2.1.0]pentane (7).

Bicyclo[2.1.0]pentane-2-spirocyclopropane (8). Benzylmercuriodomethane⁶ (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 C₇H₁₀, 94.078) and ¹H 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 diazomethane⁷ 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 chamber¹¹ 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 ¹H 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 plot⁹ of ln ln (1/[5]) against T(K)⁻¹ gave 36 kcal/mol as an estimate for E_a.

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

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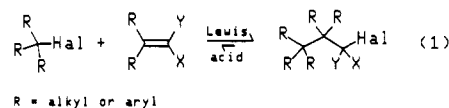
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The construction of quaternary carbon centers often requires a special methodology since many of the transformations that are frequently employed for carbon-carbon bond formations are not applicable to the efficient creation

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.

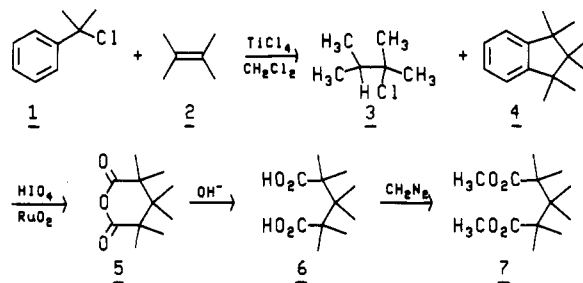
In several instances, quaternary carbon centers have been generated by reactions proceeding via tertiary carbenium ions. Examples are the *tert*-alkylations of carbonyl compounds,² reactions of *tert*-alkyl halides with alkylaluminum^{3a} or alkyltitanium compounds,^{3b} geminal dimethylations of ketones,^{3c} 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.



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 TiCl₄ (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 hexamethylindane (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 acyclic intermediates (geminal dialkyl effect⁸), and precursors of 4 are not detectable.



Oxidation of 4 with NaIO₄/RuO₂ in CCl₄/CH₃CO₂H/H₂O gave 64% of the anhydride 5, which was hydrolyzed

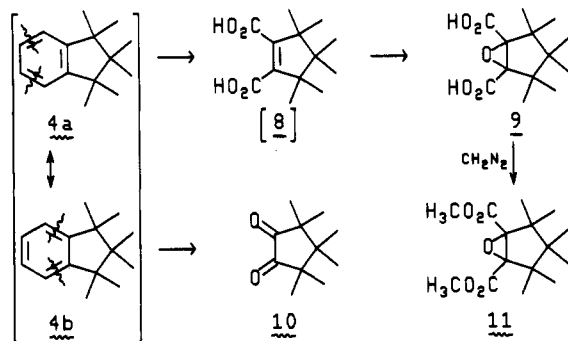
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with a 1:1 mixture of 40% aqueous KOH and 2-propanol. Treatment of the diacid **6** with diazomethane gave the diester **7**, and the anhydride **5** was recovered when **6** was warmed in $\text{CF}_3\text{CO}_2\text{H}$.

The oxidation of **4** was also achieved when $\text{NaIO}_4/\text{RuO}_2$ was employed in $\text{CCl}_4/\text{CH}_3\text{CN}/\text{H}_2\text{O}$,^{9a} but under these conditions more side products were formed, and the reaction was approximately 3 times slower than in the $\text{CCl}_4/\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{O}$ mixture. In view of the previously postulated inactivation of the ruthenium catalyst by carboxylic acids,^{9a} it is surprising that we find $\text{CH}_3\text{CO}_2\text{H}$ to be a more efficient cosolvent than CH_3CN . Carbon tetrachloride is essential for the oxidation, however, since **4** was oxidized much slower when the reaction was carried out in a $\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{O}$ mixture.

Compound **4** could neither be oxidized with $\text{NaIO}_4/\text{RuO}_2$ in the originally published solvent mixture $\text{CCl}_4/\text{H}_2\text{O}$ ^{9b} nor in the recently recommended solvent system $\text{CCl}_4/\text{DMF}/\text{H}_2\text{O}$.^{9c} Attempts to replace NaIO_4 by NaOCl ¹⁰ or $\text{Na}_2\text{S}_2\text{O}_8$ in the above oxidation mixtures have also not been successful. Only chlorination of the aromatic ring of **4** took place with freshly prepared NaOCl following Dressel's procedure.^{10d} Oxidations of **4** with H_2O_2 in $\text{CF}_3\text{CO}_2\text{H}$ ¹¹ gave complex mixtures of products containing up to 22% of the anhydride **5**.

During optimization of the oxidation conditions, we have worked up a mixture obtained by incomplete oxidation of **4** with $\text{NaIO}_4/\text{RuO}_2$ in $\text{CCl}_4/\text{CH}_3\text{CN}/\text{H}_2\text{O}$. Apart from nonreacted indan **4** (18%) and the anhydride **5** (19%), the epoxide **9** (19.5%) and the diketone **10** (11%) have been isolated. Their formation can be deduced from the two resonance structures **4a** and **4b** with the nonobserved acid **8** as precursor of **9**. Further oxidation of **9** and **10** to give the anhydride **5** is thinkable, but has not been proven.



According to force field calculations (MMPMI),¹² the most stable conformation of **7**, which is characterized by dihedral angles $\text{O}-\text{C}(1)-\text{C}(2)-\text{C}(3)$ of about 90° , incorporates a strain energy of 17.9 kcal/mol to give a ΔH_f° value of -224.0 kcal/mol. The splitting of the ^{13}C NMR resonance at δ 24.04 below -80°C (100 MHz) is explained by the nonequivalence of the methyl groups at C-2/C-4 in this conformation.

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Experimental Section

General Procedures. IR spectra were recorded on a Shimadzu IR-435 spectrometer. NMR spectra were taken on a Varian XL 200 and a JEOL JNM-GX 400 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded on a 70-250 VG spectrometer, and the microanalyses were carried out by Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach. 2-Chloro-2-phenylpropane (**1**) was obtained by passing dry HCl through a 10% solution of α -methylstyrene in pentane at -30°C .¹³

1,1,2,2,3,3-Hexamethylindan (4). Compound **1** (82.8 g, 0.535 mol), 2,3-dimethyl-2-butene (**2**) (110 g, 1.31 mol), and 1.6 L of CH_2Cl_2 (distilled over P_2O_5) were placed into a four-necked 2-L flask, equipped with an efficient stirrer, thermometer, drying tube, and a rubber septum. The mixture was cooled at -75°C , and 10 mL of TiCl_4 was added with a syringe during 10 min. After 1 h of stirring, the orange mixture was poured into a solution of 300 mL of hydrochloric acid and 600 mL of water. The organic layer was dried over MgSO_4 , and the solvent was evaporated under reduced pressure. Vacuum distillation gave 78.2 g (72%) of colorless **4**, bp $52-55^\circ\text{C}$ (0.5 mbar): IR (neat) 3085, 3035, 3000, 2980, 2890, 1490, 1460, 1390, 1320, 1120, 1040, 760 cm^{-1} ; ^1H NMR (CCl_4) δ 0.88 (s, 6 H), 1.20 (s, 12 H), 7.03 (s, 4 H); ^{13}C NMR (CDCl_3) δ 21.48 (q), 27.39 (q, double intensity), 47.53 (s, double intensity), 48.29 (s), 122.40 (d), 126.59 (d), 150.19 (s); mass spectrum (70 eV), m/z (relative intensity) 202 (M^+ , 23), 187 (100), 145 (83), 131 (27), 117 (16). Anal. Calcd for $\text{C}_{15}\text{H}_{22}$ (202.3): C, 89.04; H, 10.96. Found: C, 88.98; H, 11.07.

3,3,4,4,5,5-Hexamethyltetrahydropyran-2,6-dione (5). Indan **4** (0.41 g, 2.0 mmol), NaIO_4 (12.8 g, 60 mmol), $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (0.045 g, 0.266 mmol), CCl_4 (8 mL), acetic acid (12 mL), and 36 mL of water were stirred and heated at reflux for 24 h. After adding 25 mL of water, the mixture was extracted with five 20-mL portions of ether. The combined extracts were washed with aqueous NaHCO_3 solution and dried with MgSO_4 . Evaporation of solvent afforded 0.288 g of crude **5** as a waxy solid, which can be used for the preparation of **6** without further purification. According to GC analyses (column temperature 220°C), this material contained 89% of **5** (total yield 64%). Sublimation ($80^\circ\text{C}/0.5$ mbar) or crystallization afforded pure **5** with mp $174-175^\circ\text{C}$ (EtOH): IR (KBr) 2979, 1798, 1750, 1480, 1464, 1451, 1388, 1281, 1236, 1202, 1153, 1128, 1029, 1003, 736, 642 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (s, 6 H), 1.35 (s, 12 H); ^{13}C NMR (CDCl_3) δ 20.55 (q), 24.13 (q, double intensity), 38.48 (s), 47.03 (s, double intensity), 173.53 (s); mass spectrum (70 eV), m/z (relative intensity) 199 ($\text{M}^+ + 1$, 2), 171 (3), 149 (7), 129 (3), 111 (8), 97 (8), 95 (5), 84 (100), 71 (13), 70 (41), 69 (60), 57 (26), 56 (8), 55 (21). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3$ (198.3): C, 66.64; H, 9.15. Found: C, 66.77; H, 9.07.

Hexamethylglutaric Acid (6). Compound **5** (2.82 g, 14.2 mmol), 45 mL of 40% aqueous NaOH, and 45 mL of 2-propanol were stirred at ambient temperature for 14 h. The mixture was diluted with 50 mL of water and extracted with three 50-mL portions of ether. The water layer was then stirred with charcoal, filtered, and acidified with hydrochloric acid. The colorless precipitate was collected, washed with water, and dried in vacuo to give 2.81 g (91%) of **6** with mp $187-188^\circ\text{C}$ dec. Extraction of the filtrate with ether afforded 0.30 g of less pure material. An analytical sample was recrystallized from methanol: mp $188-189^\circ\text{C}$ dec; IR (KBr) 3400 and 3050 (broad OH), 2982, 2879, 2632, 2547, 1689, 1480, 1457, 1409, 1384, 1295, 1198, 1150, 1136, 1089, 957 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.21 (s, 6 H), 1.32 (s, 12 H); ^{13}C NMR (CDCl_3) δ 21.70 (q), 25.07 (q, double intensity), 44.26 (s), 49.08 (s, double intensity), 184.74 (s). Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_4$ (216.3): C, 61.09; H, 9.32. Found: C, 60.89; H, 9.16.

Dimethyl Hexamethylglutarate (7). A few drops of methanol and 5 mL of an ethereal solution of diazomethane¹⁴ were added to 32.2 mg (0.149 mmol) of **6** to give a yellow solution, which decolorized on standing overnight. The solvents were evaporated in vacuo, and the residue was distilled by bulb-to-bulb distillation, affording 31.5 mg (87%) of a colorless, viscous liquid, bp 90°C (bath)/0.55 mbar: IR (neat) 2972, 2941, 1724, 1458, 1431, 1384, 1264, 1191, 1158, 1126, 1110, 1096 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.14

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(s, 6 H), 1.21 (s, 12 H), 3.64 (s, 6 H); ^{13}C NMR (CDCl_3) δ 21.99 (q), 24.04 (q, double intensity), 44.08 (s), 49.28 (s, double intensity), 51.47 (q), 178.16 (s); mass spectrum (70 eV), m/z (relative intensity) 213 ($\text{M}^+ - \text{OCH}_3$, 8), 185 (15), 143 (36), 111 (11), 102 (75), 83 (63), 73 (100), 55 (18), 41 (35). Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_4$ (244.3): C, 63.91; H, 9.90. Found: C, 63.97; H, 10.11.

Partial Oxidation of 4. Compound 4 (0.81 g, 4.0 mmol), NaIO_4 (12.8 g, 60 mmol), $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (20 mg, 0.12 mmol), acetonitrile (16 mL), CCl_4 (12 mL), and 24 mL of water were stirred at ambient temperature for 26 h. After adding 50 mL of water the mixture was extracted with five 25-mL portions of CH_2Cl_2 . The combined extracts were dried over MgSO_4 and filtered, and CH_2Cl_2 was evaporated under reduced pressure. The residue was dissolved in ether and filtered. The filtrate was extracted with aqueous sodium bicarbonate solution, and the two layers were worked up separately.

The organic layer was dried over MgSO_4 , filtered, and concentrated under reduced pressure to give 0.264 g of a neutral product. According to GC analysis (4 m column 20% GE SE 30 on Chromosorb W AW DMCS 80-100 mesh, 220 °C column temperature), this product contained **10** (t_R 5.55 min, 30%), **4** (t_R 6.87 min, 5.5%), and **5** (t_R 7.77 min, 59%). Compound **10** (47 mg) was isolated from this mixture by medium-pressure liquid chromatography (RP 18, methanol/water, 95:5). **3,3,4,4,5,5-Hexamethylcyclopentane-1,2-dione (10)**:¹⁵ IR (neat) 2966, 2872, 1750, 1738, 1475, 1459, 1454, 1382, 1276, 1145, 1099, 1060, 1032, 984 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.98 (s, 6 H), 1.20 (s, 12 H); ^{13}C NMR (CDCl_3) δ 20.69 (q), 21.88 (q, double intensity), 39.85 (s), 48.44 (s, double intensity), 208.95 (s); mass spectrum (70 eV), m/z (relative intensity) 182 (M^+ , 14), 84 (100), 70 (21), 69 (47), 57 (11), 55 (9), 43 (16), 42 (9), 41 (27).

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The sodium bicarbonate washings were stirred with charcoal, filtered, acidified with hydrochloric acid, and extracted with ether. The ether extracts were dried over MgSO_4 , filtered, and evaporated in vacuo to give a mixture of carboxylic acids. Esterification was carried out by adding 2 mL of methanol and 15 mL of an ethereal solution of CH_2N_2 .¹⁴ The yellow solution was left under the hood overnight and concentrated under reduced pressure to yield 0.335 g of a mixture of methyl esters. GC analysis (230 °C column temperature, other conditions see above) indicated the following composition of the mixture: **7** (t_R 7.1 min, 6%), **11** (t_R 11.5 min, 67%), and two unidentified compounds with retention times of 15.6 and 19.1 min. Compound **11** (154 mg) was isolated from this mixture by medium-pressure liquid chromatography (RP 18, methanol/water, 85:15). **1,5-Bis(methoxycarbonyl)-2,2,3,3,4,4-hexamethyl-6-oxabicyclo[3.1.0]hexane (11)**: viscous oil; bp 145 °C (bath)/0.7 mbar; IR (neat) 2945, 1740, 1439, 1380, 1303, 1278, 1240, 1208, 1125, 1061, 1045, 810 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.77 (s, 3 H), 0.98 (s, 3 H), 1.09 (s, 6 H), 1.26 (s, 6 H), 3.75 (s, 6 H); ^{13}C NMR (CDCl_3) δ 20.94 (q, double intensity), 21.57 (q), 23.71 (q, double intensity), 26.75 (q), 44.79 (s, double intensity), 45.83 (s), 52.25 (q), 74.86 (s), 166.54 (s); mass spectrum (70 eV), m/z (relative intensity) 284 (M^+ , 17), 269 (29), 241 (24), 225 (25), 193 (44), 165 (60), 155 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_5$ (284.4): C, 63.36; H, 8.51. Found: C, 62.90; H, 8.56.

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Registry No. 1, 934-53-2; 2, 563-79-1; 3, 594-57-0; 4, 91324-94-6; 5, 115942-54-6; 6, 115942-55-7; 7, 115942-56-8; 9, 115942-57-9; 10, 16980-19-1; 11, 115942-58-0.

Communications

Radical Cyclizations in Conformationally Restrained Systems. Generation of the *cis,cis*-Hexahydrophenanthro(4,5-*bcd*)furan Tetracycle of Morphine

Summary: Tandem radical cyclization converts an appropriately substituted phenyl cyclohexenyl ether **1** to the *cis,cis* tetracyclic morphine model **2b** and its epimer **2a**. The stereochemical relationships in each isomer were determined by analysis of ^1H NMR decoupling and NOE experiments.

Sir: Radical reactions have generally been perceived as lacking in stereochemical predictability.² The requirement for stereoselectivity in the addition of a radical to an olefin may be simply stated (only one face of each prochiral center, either radical or olefinic carbon, can be available for reaction) but it is not easily fulfilled. Notable exceptions are those radical cyclizations leading to 5,5- or 5,6-*cis*-fused ring systems^{2,3} in which reactive centers are subject to the conformational constraint of the short tether. Striking successes in the application of this methodology and its tandem variant for the synthesis of quinane⁴ and

indane⁵ natural products have been reported.

The use of radical cyclizations for the preparation of ring systems other than 5,5- or 5,6-*cis* fused has not been extensive.⁶ Formation of larger rings may suffer from competitive side reactions⁷ as well as uncertain stereochemical results. It seems plausible, however, that radicals generated with the proper spatial orientation in conformation-

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