**Photolysis of 5c.** A solution of **5c** (230 mg, 6.00 mmol) in benzene (250 mL) under argon was irradiated with a 450-W medium pressure mercury lamp (Pyrex filter) for 50 min. The reaction mixture was concentrated in vacuo, and the residue was purified via chromatography on silica gel by using 15% ethyl acetae–hexane mixed solvent as elutent. Compound **12** (30 mg, 14%) was isolated from the first chromatography fractions as a colorless oil: IR (KBr) 2961 (s), 1749 (s), 1390 (m), 1324 (s), 1313 (s), 1222 (s), 1169 (s); $^1H$ NMR ($CDCl_3$) $\delta$ 1.54 (*A*B, $J_{AB}$ = 12.0 Hz, 1 H), 1.62 (A*B*, $J_{AB}$ = 12.0 Hz, 1 H), 2.16 (s, 3 H), 2.28–2.53 (m, 2 H), 2.40 (s, 3 H), 2.60–2.78 (m, 2 H), 3.20–3.43 (m, 2 H), 5.75 (s, 1 H), 6.64 (s, 1 H), 7.29 (*A*B, $J_{AB}$ = 7.9 Hz, 2 H), 7.24 (A*B*, $J_{AB}$ = 7.9 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.31 (q), 21.39 (q), 31.79 (t), 44.08 (d), 47.70 (d), 48.65 (d), 49.35 (d), 61.61 (d), 66.44 (d), 115.54 (d), 128.15 (d), 129.79 (d), 137.32 (s), 144.25 (s), 148.04 (d), 151.51 (s), 157.86 (s), 168.88 (s). Anal. Calcd for $C_{20}H_{20}O_4S$: $M_r$ 356.1083. Found (high-resolution mass spectrometry): $M_r$ 356.1066.

Continued elution of the chromatography column afforded **11b** (110 mg, 52%). Recrystallization of this material from diethyl ether afforded pure **11b** as a colorless microcrystalline solid: mp 132–133 °C; IR (KBr) 2986 (s), 1729 (s), 1320 (s), 1310 (s), 1257 (s), 1243 (s), 1163 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 1.61 (*A*B, $J_{AB}$ = 10.7 Hz, 1 H), 1.70 (A*B*, $J_{AB}$ = 10.7 Hz, 1 H), 2.05 (s, 3 H), 2.42 (s, 3 H), 2.60–3.48 (m, 8 H), 7.30 (*A*B, $J_{AB}$ = 8.2 Hz, 2 H), 7.80 (A*B*, $J_{AB}$ = 8.2 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.84 (q), 21.40 (q), 40.18 (t), 42.31 (d), 46.68 (d), 47.41 (d), 48.24 (d), 48.70 (d), 49.14 (d), 50.52 (d), 52.70 (d), 75.49 (s), 90.81 (s), 128.93 (d), 129.57 (s), 135.54 (s), 144.63 (s), 169.06 (s). Anal. Calcd for $C_{20}H_{20}O_4S$: Calcd. C, 67.40; H, 5.66. Found: C, 67.32; H, 5.65.

**Independent Synthesis of 12.**[11] Compound 8 (100 mg, 0.318 mmol) and $TsOH{\cdot}H_2O$ (15 mg, 0.079 mmol) were dissolved in isopropenyl acetate (20 mL, excess). The mixture was heated at such a rate that excess isopropenyl acetate could be removed by slow distillation during 3 h. The residue was allowed to cool to room temperature, and the reaction was quenched by addition of 10% aqueous $NaHCO_3$ (30 mL). The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed sequentially with 10% aqueous $NaHCO_3$ (30 mL) and water (2 × 30 mL), dried ($Na_2SO_4$), and filtered. The filtrate was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by using 15% ethyl acetate–hexane mixed solvent as eluent. Compound **12** (30 mg, 26%) was thereby obtained as a colorless oil. The IR, $^1H$ NMR, and $^{13}C$ NMR spectra of this material were identical in all respects with the corresponding spectra of **12b** that had been isolated previously as one of the products formed via photolysis of **5c**. Continued elution of the chromatography column resulted in recovery of unreacted **7** (45 mg, 45%).

**Control Experiment: Photolysis of 12.** A solution of **12** (30 mg, 0.084 mmol) in benzene (250 mL) under argon was irradiated with a 450-W medium pressure mercury lamp (Pyrex filter) for 50 min. The reaction mixture was concentrated in vacuo, and the residue was purified via chromatography on silica gel by using 15% ethyl acetate–hexane mixed solvent as eluent. Unreacted **12** was recovered (11 mg, 37%) along with a minute quantity of unidentified material. Importantly, **11b** was not isolated from this reaction, nor could its presence be detected via thin layer chromatographic analysis or via analysis of the $^1H$ NMR or $^{13}C$ NMR spectra of the reaction products.

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**Supplementary Material Available:** Figures 2–5 (structure drawings of **5a**, **6**, **9**, and **11a**, respectively), Tables I–V, VI–X, XI–XV, and XVI–XX (tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates, and isotropic thermal parametes for **5a**, **6**, **9**, and **11a**, respectively), discussion of bond lengths in the X-ray structures of **6** and **11a**, and description of the experimental method used to determine the X-ray crystal structures of **5a**, **6**, **9**, and **11a** (29 pages). Ordering information is given on any current masthead page.

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# Pinacol Condensation of Homocubanone. Synthesis and Chemistry of Homocubylidenehomocubane

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Reductive coupling of homocubanone (1) with $TiCl_4$–Zn afforded the corresponding pinacol (**3**, 21%) and homocubanol (**4**, 40%). Reaction of **3** with $HC(OEt)_3$ in the presence of benzoic acid afforded cyclic orthoformate **5** (95%), which when heated with benzoic acid at 200 °C gave homocubylidenehomocubane (**2**, 95%). When treated with $AgNO_3$-impregnated silica gel at 25 °C for 6 days, **2** gradually underwent homocubane–norsnoutane rearrangement, thereby affording **7**. Acid-promoted pinacol rearrangement of **3** gave the corresponding pinacolone **6** (61%). Electrophilic addition of trifluoroacetic acid and of bromine to the C=C double bond in **2** proceeded in both cases via simple 1,2-addition (i.e., without accompanying Wagner–Meerwein rearrangement), thereby affording **8** (64%) and **9** (24%), respectively. The structures of **2**, **6**, **7**, and **9** were elucidated via X-ray crystallographic methods. The results of MM2 calculations suggest that there is insufficient driving force provided by relief of steric strain to promote Wagner–Meerwein rearrangement of the carbocation that is produced upon protonation of the C=C double bond in **2**.

## Introduction

The synthesis and chemistry of novel, highly strained polycyclic "cage" compounds have attracted considerable attention in recent years.[1] Many compounds that are members of this class possess unusual symmetry properties that render them aesthetically pleasing.[2] Cage molecules, due to their compact structures, often possess unusually high densities. In addition, there is considerable strain energy contained within carbocyclic cage systems that are composed of four- and five-membered rings. Accordingly,

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(1) For reviews, see: (a) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT, 1989; Vol. 1, pp 357–399. (b) Griffin, G. W.; Marchand, A. P. *Chem. Rev.* 1989, *89*, 997. (c) Marchand, A. P. *Chem. Rev.* 1989, *89*, 1011.

(2) Nakazaki, M. *Top. Stereochem.* 1984, *15*, 199.

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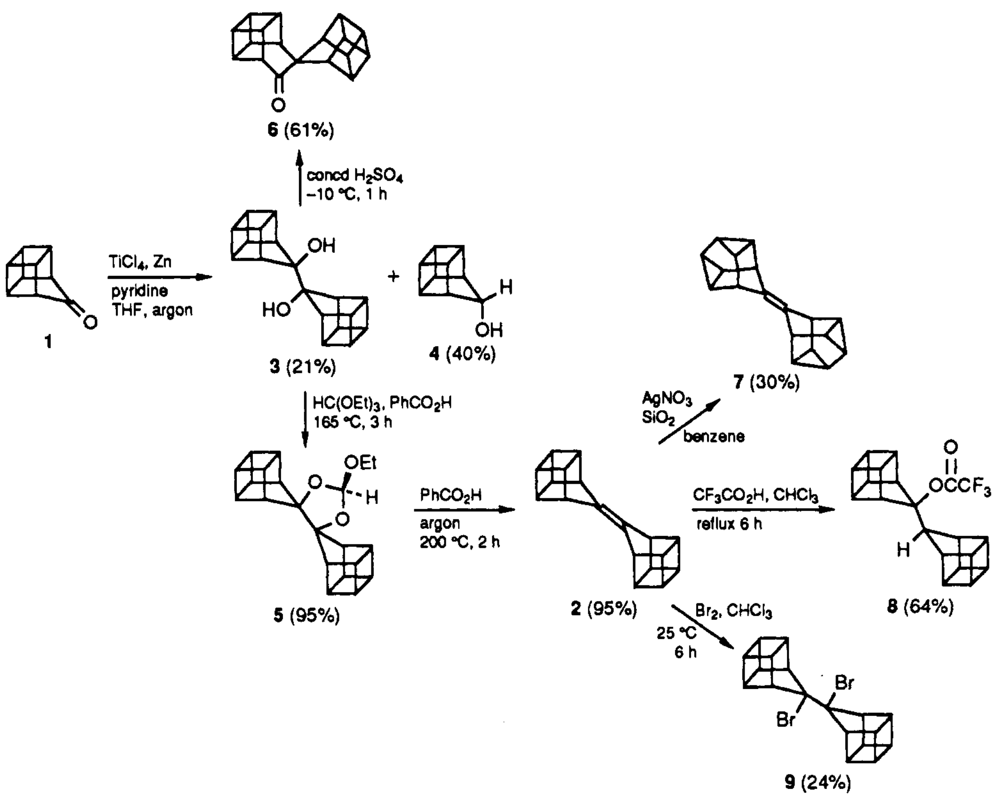
**Scheme I**



such compounds are of interest as potential high density/high energy fuels.[3] Finally, polynitro derivatives of these systems have attracted attention as a new class of explosives and propellants.[4]

As part of a continuing study of the synthesis and chemistry of novel polycyclic systems,[1a] we have examined titanium-promoted reductive dimerization of homocubanone[5] (1). This reaction was of interest as a potentially useful route for synthesizing homocubylidenehomocubane (2), whose expected[6] high density and high strain energy content render this compound of interest as a candidate fuel system.[3]

**Reductive Dimerization of 1 and Related Studies.** Reductive coupling of ketones with low-valent titanium generally leads to the formation of the corresponding dimeric alkene.[7] The reaction is believed to proceed via the intermediate pinacol, which subsequently undergoes titanium-induced deoxygenation to the corresponding alkene.[7] In our hands, reaction of 1 with $TiCl_3$–Zn[8] afforded the corresponding pinacol (3, 21%) along with homocubanol (4, 40%, Scheme I). The structure of the pinacol was established via analysis of its $^{1}$H and $^{13}$C NMR spectra. The proton noise-decoupled $^{13}$C NMR spectrum of 3 displayed only five resonances, consistent with the fact that 3 possesses two twofold symmetry elements.

Despite several attempts, we were unable to promote titanium-induced deoxygenation of 3. As an alternative, 3 was heated (165 °C) with triethyl orthoformate in the presence of benzoic acid, thereby affording the corresponding cyclic orthoformate 5 in 95% yield.[9] Excess triethyl orthoformate was removed, and the residual orthoformate ester 5 was heated strongly with benzoic acid (200 °C). This procedure afforded 2 in excellent yield (95% from 5, ca. 20% overall from homocubanone). The proton noise-decoupled $^{13}$C NMR spectrum of 2 contained only four absorption lines, consistent with the suggested structure.

Unequivocal confirmation of the structure of 2 was secured via single-crystal X-ray structural analysis. A particularly interesting feature of 2 is the unusually high values of its crystal density as calculated from unit cell parameters, i.e., 1.38 g·cm$^{-3}$ (see Table II in supplementary material).

It was of interest to study the acid-promoted pinacol rearrangement of 3. Thus, treatment of 3 with concentrated sulfuric acid at −10 °C afforded the corresponding pinacolone (i.e., spiro ketone 6) in 61% yield. Compound 6 contains spirocyclic basketanone and homocubane moieties. The spirocyclic nature of 6 is confirmed by the presence of a quaternary carbon resonance at $\delta$ 67.77 in its $^{13}$C NMR spectrum. The structure of 6 was established unequivocally by X-ray crystallographic methods (see supplementary material).

**Ag(I)-Promoted Rearrangement of 2.** Homocubane is known to undergo Ag(I)-promoted rearrangement to norsnoutane.[10] It was of interest to determine whether a similar homocubane–norsnoutane rearrangement would occur in 2 or if Ag(I) would react preferentially with the C=C double bond in this substrate. In fact, the former process occurred when a benzene solution of 2 was treated

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(3) Burdette, G. W.; Lander, H. R.; McCoy, J. R. *J. Energy* **1978**, *2*, 289.

(4) For a review, see: Marchand, A. P. *Tetrahedron* **1988**, *44*, 2377.

(5) (a) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3860. (b) Mehta, G.; Srikrishna, A.; Suri, S. C. *Ibid.* **1980**, *45*, 5375.

(6) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; Chapter 1.

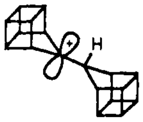
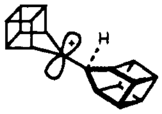
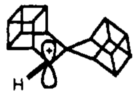
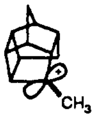
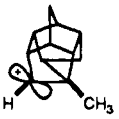
(7) (a) See: McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405 and references cited therein. (b) Lenoir, D. *Synthesis* **1989**, 883.

(8) Lenoir, D. *Synthesis* **1977**, 553.

(9) (a) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1964**, *17*, 1392. (b) Josan, J. S.; Eastwood, F. W. *Ibid.* **1968**, *21*, 2013.

(10) (a) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 281. (b) Ōsawa, E.; Schleyer, P. v. R.; Chang, L. W. K.; Kane, V. V. *Tetrahedron Lett.* **1974**, 4174. (c) Paquette, L. A.; Ward, J. S.; Boggs, R. A.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 1101. (d) Paquette, L. A.; Boggs, R. A.; Ward, J. S. *Ibid.* **1974**, *97*, 1118.

**Table I. MM2[15] Calculations for Carbocations 10a, 10b, 11a, and 11b**

| | <br>**10a** | <br>**10a′** (rotated 90°) | <br>**10b** | <br>**11a** | <br>**11b** |
|---|---|---|---|---|---|
| $\Delta H_f$ (kcal/mol) | 390.28 | 391.43 | 403.87 | 210.43 | 201.47 |
| $E$(strain) (kcal/mol) | 237.01 | 238.16 | 229.87 | 56.99 | 36.81 |

with silver nitrate impregnated silica gel at room temperature for 6 days. The structure of the rearrangement product 7 was elucidated by single-crystal X-ray structural analysis (see supplementary material).

Two bands were observed in the C=C double bond (stretching vibration) region of the Raman spectrum of 7, i.e., at 1733 and 1744 cm$^{-1}$. The fact that two bands are observed rather than one may be due to Fermi resonance that arises via coupling of the C=C stretching vibration in 7 with an overtone or combination band.[11] A likely candidate in this regard is an overtone of an intense band in the Raman spectrum of 7 that occurs at 897 cm$^{-1}$. By way of contrast, the C=C stretching vibration in the Raman spectrum of 2 appears as a single sharp band at 1728 cm$^{-1}$.

**Electrophilic Addition to the C=C Double Bond in 2.** As part of a continuing study of electrophilic additions to strained C=C double bonds,[12] the corresponding addition of trifluoroacetic acid to the C=C moiety in 2 was investigated. When a solution of 2 and trifluoroacetic acid in chloroform was refluxed for 6 h, an adduct, 8, was obtained in 64% yield (Scheme I). The proton noise-decoupled $^{13}$C NMR spectrum of 8 indicates the presence of 12 nonequivalent carbon atoms. In addition, the corresponding off-resonance decoupled spectrum displays a singlet at $\delta$ 109.5. These results suggest that 8 was formed via simple 1,2-addition of trifluoroacetic acid to the C=C double bond in 2. Apparently, Wagner–Meerwein rearrangement does not compete effectively with 1,2-addition of the electrophile to the C=C moiety in this system.

Polar addition of bromine to the C=C double bond in 2 was also studied. A single adduct was formed when 2 was reacted with $Br_2$–$CHCl_3$ solution at room temperature for 6 h. The proton noise-decoupled $^{13}$C NMR spectrum of the product thereby obtained (i.e., 9, Scheme I) contains only five resonances. The corresponding off-resonance decoupled spectrum displays a singlet at $\delta$ 93.79. These results suggest that once again simple 1,2-addition of the electrophile to the C=C double bond in 2 has occurred. The fact that addition of bromine to 2 occurred without concomitant Wagner–Meerwein rearrangement was confirmed via X-ray crystallographic methods (see supplementary material).

Due to the symmetry inherent in system 2, it is not possible to deduce the stereochemistry of electrophilic addition (i.e., syn or anti) across the C=C double bond simply from knowledge of the structure of the adduct. However, by analogy to the course of electrophilic bromination of adamantylideneadamantane,[13] it is likely that bromination of 2 proceeds stereospecifically anti via the corresponding bromonium ion.[13,14]

**Results of Molecular Mechanics Calculations.** In an effort to gain further insight into the nature of this electrophilic addition reaction, MM2[15] calculations have been performed on the carbocation 10a derived via addition of H$^+$ to the C=C bond in 2. The results, shown in Table I, indicate that ca. 8 kcal/mol of strain energy is released upon Wagner–Meerwein rearrangement of carbocation 10a to carbocation 10b. However, this process results in concomitant rearrangement of a tertiary carbocation to a secondary carbocation. Apparently, the ca. 8 kcal/mol that is gained by relief of strain is insufficient to offset the loss in stabilization energy that would result via Wagner–Meerwein rearrangement of tertiary carbocation 10a to the (less stable) secondary carbocation 10b.

For comparison, MM2[15] calculations have been performed for the corresponding Wagner–Meerwin rearrangement of 8-methylpentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecyl carbocation (11a). This carbocation has been shown experimentally to undergo spontaneous Wagner–Meerwein rearrangement to the corresponding, substituted $D_3$-trishomocubyl carbocation 11b.[16] The results (Table I) indicate that Wagner–Meerwein rearrangement of tertiary carbocation 11a to secondary carbocation 11b proceeds with ca. 20 kcal/mol relief of strain energy. We conclude from this exercise that the minimum driving force required to promote Wagner–Meerwin rearrangement of a tertiary carbocation to the corresponding secondary carbocation must be greater than ca. 8 kcal/mol but less than ca. 20 kcal/mol.[17]

## Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE.

**9-[9′-Hydroxy-9′-homocubyl]homocuban-9-ol (3).** To dry tetrahydrofuran (THF, 70 mL), which was cooled externally to 0 °C, was added dropwise with stirring $TiCl_4$ (7.50 g, 39.9 mmol). The resulting solution was stirred at 0 °C for 10 min. An argon atmosphere was introduced into the reaction flask, and powdered zinc (1.72 g, 36.4 mmol) then was added portionwise. The cold

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(14) Ruasse, M.-F. *Acc. Chem. Res.* **1990**, *23*, 87.

(15) (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*, ACS Monograph No. 177; American Chemical Society: Washington, DC, 1982. (b) MM2 calculations were performed by using PCMODEL, available from Serena Software, Box 3076, Bloomington, IN 47402. MM2 parameters for carbocations were taken from Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Molecular Modeling*: Liotta, D., Ed.; JAI Press: Greenwich, CT, in press.

(16) Dekker, T. G.; Oliver, D. W.; Venter, A. *Tetrahedron Lett.* **1980**, *21*, 3101.

(17) (a) The data in Table I indicate that $\Delta\Delta H_f$ is endothermic by ca. 13 kcal/mol upon proceeding from **10a** to **10b**, but this quantity is exothermic by ca. 9 kcal/mol when going from **11a** to **11b**. A referee has pointed out that these data alone may account for our observations. (b) In addition, our conclusion is consistent with the results of calorimetric studies that indicate that rearrangement of *sec*-butyl to *tert*-butyl carbocation is exothermic by 14.2 kcal/mol. See: (a) Bittner, E. W.; Arnett, E. M.; Saunders, M. *J. Am. Chem. Soc.* **1976**, *98*, 3734. (b) Arnett, E. M.; Petro, C. *Ibid.* **1978**, *100*, 5408. (c) Arnett, E. M.; Pienta, N.; Petro, C. *Ibid.* **1980**, *102*, 398.

bath was removed, and the resulting black reaction mixture was stirred at room temperature under argon for 2 h. To the reaction mixture was added pyridine (0.8 mL) dropwise with stirring, whereupon the black precipitate dissolved. The resulting homogeneous solution was warmed to 60 °C and was stirred at that temperature for 0.5 h. The reaction was allowed to cool slowly to room temperature, and a solution of 1[5] (4.5 g, 32 mmol) in dry THF (30 mL) was added. The resulting mixture was refluxed for 0.5 h and then allowed to cool. To the cooled reaction mixture was added 20% aqueous $Na_2CO_3$ (40 mL), and the mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed sequentially with water (20 mL) and with brine (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo, thereby affording crude 3 (5.2 g). The crude product was purified by column chromatography on silica gel (5% EtOAc–hexane mixed solvent as eluent). The following products were thereby obtained: homocubanol (4, 1.8 g, 40%) as a colorless microcrystalline solid: [mp 160–163 °C (lit.[18] mp 167–168 °C)] and diol 3 (950 mg, 21%) as a colorless microcrystalline solid [mp 218–219 °C; IR (KBr) 3400 (s), 2900 (s), 1240 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.78 (br s, 2 H), 2.98 (m, 8 H), 3.35 (m, 4 H), 3.50 (m, 4 H): $^{13}C$ NMR ($CDCl_3$) $\delta$ 40.26 (d), 43.58 (d), 44.36 (d), 49.49 (s), 97.68 (s). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77. Found: C, 81.11; H, 6.77].

**Reaction of 3 with Triethyl Orthoformate.** A mixture of diol 3 (140 mg, 0.54 mmol), triethyl orthoformate (1 mL, excess), and benzoic acid (5 mg) was heated at 165 °C for 3 h. Excess triethyl orthoformate was removed by distillation, and the reaction mixture was allowed to cool slowly to room temperature. The reaction mixture was stirred with 10% aqueous $Na_2CO_3$ (10 mL) and then was extracted with ethyl acetate (3 × 30 mL). The organic layer was washed sequentially with water (10 mL) and with brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue, 5 (155 mg, 95%), a gummy semisolid, was used as obtained without further purification.

**Homocubylidenehomocubane (2).** An intimate mixture of 5 (80 mg, 0.25 mmol) and benzoic acid (3 mg) was heated under argon at 200 °C for 4 h. The reaction mixture was then allowed to cool slowly to room temperature, and 10% aqueous $Na_2CO_3$ (10 mL) was added. The resulting mixture was extracted with $CHCl_3$ (3 × 40 mL). The combined organic extracts were washed sequentially with water (15 mL) and with brine (15 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo, thereby affording 2 (55 mg, 95%). Recrystallization from toluene afforded analytically pure 2 as a colorless microcryststalline solid: mp 279–280 °C; Raman (solid sample in capillary tube) 1736 $cm^{-1}$ (s); $^1H$ NMR ($C_6D_6$) $\delta$ 3.20 (m, 4 H), 3.45 (m, 8 H), 3.70 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 41.63 (d), 44.56 (d), 44.58 (d), 140.98 (s). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.93; H, 6.99.

**10-Oxospiro[pentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]decane-9,9′-pentacyclo[4.3.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]nonane (6).** A solution of 3 (120 mg, 0.451 mmol) in $CH_2Cl_2$ (3 mL) was cooled to −10 °C via an ice–salt bath. To this cold solution was added concentrated $H_2SO_4$ (2 mL), and the resulting mixture was stirred vigorously at −10 °C for 1 h. The reaction was quenched via careful, portionwise addition of crushed ice (8 g), and the reaction mixture was extracted with $CH_2Cl_2$ (4 × 20 mL). The combined organic extracts were washed sequentially with 5% aqueous $NaHCO_3$ (3 mL), water (5 mL), and brine (5 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by passage through a short silica gel chromatography column (5% ethyl acetate–hexane mixed solvent as eluent). Spiro ketone 6 (70 mg, 61%) was thereby obtained as a colorless microcrystalline solid: mp 206–207 °C; IR (KBr) 2750 (s), 1650 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 3.05 (m, 8 H), 3.40 (m, 8 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 36.81 (d), 38.54 (2 C, d), 39.48 (2 C, d), 41.49 (2 C, d), 42.80 (d), 44.00 (2 C, d), 44.42 (d), 46.05 (2 C, d), 48.39 (d), 50.34 (2 C, d), 67.77 (s), 215.13 (s). Anal. Calcd for $C_{18}H_{16}O$: $M_r$ 248.1201. Found (HRMS): $M_r$ 248.1199.

**3-Tetracyclo[3.2.0.0$^{2,7}$.0$^{4,6}$]hept-3′-ylidenetetracyclo-[3.2.0.0$^{2,7}$.0$^{4,6}$]heptane (Quadricyclylidenequadricyclane, 7).** To a solution of $AgNO_3$ (200 mg, 1.18 mmol) in water (4 mL) was added silica gel (2 g). The resulting mixture was mixed throughly and then oven-dried at 140 °C for 6 h. The resulting dry, $AgNO_3$-impregnated silica gel was placed in a round bottomed flask, and a solution of 2 (60 mg, 0.26 mmol) in benzene (40 mL) was added. The reaction mixture was concentrated in vacuo, and dry benzene (5 mL) was added to the residue. The resulting mixture was stirred at room temperature for 6 days. The reaction mixture was then concentrated in vacuo, and the residue was purified by column chromatography on silica gel (benzene eluent). Compound 7 (60 mg, 100%) was thereby obtained; recrystallization from hexane afforded pure 7 as a colorless microcrystalline solid: mp 202–203 °C; Raman (solid sample in capillary tube) 1733 (w), 1744 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$) $\delta$ 1.95 (m, 8 H), 2.00 (m, 4 H), 2.75 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 37.01 (d), 38.37 (d), 42.21 (d), 140.47 (s). Anal. Calcd for $C_{18}H_{16}$: $M_r$ 232.1252. Found (high-resolution mass spectrometry): $M_r$ 232.1253.

**9-[9′-(Trifluoroacetoxy)-9′-homocubyl]homocubane (8).** A mixture of 2 (23 mg, 0.10 mmol) and trifluoroacetic acid (0.1 mL, excess) in $CHCl_3$ (5 mL) was refluxed for 6 h. The reaction mixture was allowed to cool to room temperature and was then quenched by addition of 10% aqueous $NaHCO_3$ (8 mL, excess). The resulting mixture was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic layers were washed sequentially with water (10 mL) and with brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo, thereby affording crude 8 as a yellowish solid (25 mg, 64%). Recrystallization of this material from ethyl acetate–hexane mixed solvent afforded pure 8 as a colorless microcrystalline solid: mp 95–97 °C; IR (KBr) 2970 (s), 1768 (s), 1180 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 2.70 (s, 1 H), 3.35 (m, 8 H), 3.55 (m, 8 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 40.05 (d), 41.0 (d), 42.0 (d), 43.5 (d), 43.75 (d), 45.0 (d), 46.0 (d), 49.5 (d), 57.75 (d), 109.5 (s), 114.5 (q, $^1J_{CF}$ = 120 Hz), 156.5 (q, $^2J_{CF}$ = 40 Hz). Anal. Calcd for $C_{20}H_{17}F_3O_2$: $M_r$ 346.1181. Found (high-resolution mass spectrometry): $M_r$ 346.1181.

**9-Bromo-9-(9′-bromo-9′-homocubyl)homocubane (9).** A solution of 2 (10 mg, 0.043 mmol) in $CHCl_3$ (3 mL) under argon was cooled externally to 0 °C. To this cold solution was added dropwise with stirring a solution of $Br_2$ (100 mg, 0.625 mmol, excess) in $CHCl_3$ (1 mL). After the addition was completed, the cold bath was removed. The reaction mixture was allowed to warm gradually to room temperature and then was stirred at ambient temperature for 6 h. The reaction mixture was concentrated in vacuo at room temperature, and the gummy semisolid residue (15 mg, 89%) was recrystallized from hexane. Pure 9 (4 mg, 24%) was thereby obtained as a colorless microcrystalline solid: mp 176.5–177.0 °C; IR (film) 2990 (br s), 1243 (s), 1099 (m), 1021 (m), 772 (s), 748 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 3.35–3.80 (m, 4 H), 3.39–3.44 (m, 8 H), 3.49–3.54 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 37.87 (d), 44.70 (d), 45.98 (d), 55.64 (d), 93.80 (s). Anal. Calcd for $C_{18}H_{18}Br_2$: C, 55.10; H, 4.12; Found C, 55.21; H, 4.12.

**Single-Crystal X-ray Structural Analyses of 2, 6, 7, and 9.** All X-ray data were collected on a Nicolet R3M/$\mu$ update of a $P2_1$ diffractometer by using the $\omega$-scan mode ($4° \leq 2\theta \leq 55°$), a variable scan rate, and graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71072 Å). Lattice parameters were obtained from a least-squares refinement of 25 reflections. Data were corrected for Lorentz–polarization effects, and a $\psi$-scan empirical absorption correction was applied. The structures were solved by direct methods and were refined (isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for all other atoms) by using a block-cascade least-squares technique. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + gF_0{}^2]^{-1}$. All computer programs were supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C computer configuration. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[19]

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**Registry No.** 1, 15291-18-6; **2**, 130670-16-5; **3**, 130670-17-6; **4**, 130670-18-7; **5**, 130670-19-8; **6**, 130670-20-1; **7**, 130670-21-2; **8**, 130670-22-3; **9**, 130670-23-4.

**Supplementary Material Available:** Figures 1–4 (structure drawings for **2**, **6**, **7**, and **9**, respectively), Figure 5 (22.5-MHz $^{13}$C NMR spectrum of **6**), Figure 6 (300-MHz $^1$H NMR spectrum of **9**), Table II (X-ray data for **2**, **6**, **7**, and **9**), and Tables III–VII, VIII–XII, XIII–XVII, and XVIII–XXII (tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic displacement parameters for **2**, **6**, **7**, and **9**, respectively) (27 pages). Ordering information is given on any current masthead page.

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# Synthesis of Bicyclopropyl Derivatives from the Reaction of Cyclopropylcarbene–Chromium Complexes with Alkenes

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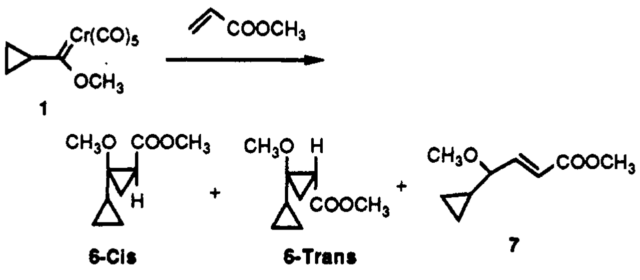
The reaction of cyclopropylcarbene–chromium complexes with alkenes has been examined. The reaction leads to cyclopropylcyclopropane derivatives in good yield, accompanied by minor amounts of ring-opened products. Conjugated dienes and $\alpha,\beta$-unsaturated esters and amides appear to be suitable substrates for the reaction. The products of the reaction are donor–acceptor substituted cyclopropanes and are further susceptible to transformations typical of this class of compounds.

## Introduction

Recently, cyclopropylcarbene–chromium complexes (**1**) have emerged as valuable reagents for organic synthesis, by coupling with alkynes to give cyclopentenones (**2**) in good to excellent yields[1] (Scheme I). During this transformation, a net ring opening of the original cyclopropane ring occurs and ethylene is expelled. At 100 °C in the absence of alkynes, carbene complex **1** does not undergo any ring-opening reaction after 1 h. The cyclopropane ring in this complex is apparently reluctant to undergo ring-opening processes. In some cases, such as when the ring is activated by the presence of alkenyl substituents (compound **3**), a facile ring-opening reaction occurs and cyclopentenone **4** is formed.[2] Since the cyclopropane rings in simple complexes such as **1** are somewhat robust, these complexes are potentially useful for cyclopropylcarbene-transfer processes.[3] Free cyclopropylcarbenes are often unstable and undergo ring-opening and/or ring-expansion processes,[4] but typically do not undergo cyclopropanation reactions with alkenes. Cationic cyclopropylcarbene–iron complexes undergo cyclopropanation reactions with electron-rich alkenes with no complications from opening of the cyclopropane ring.[5] As a possible complement to this method, we have investigated the reaction of cyclopropylcarbene–chromium complexes with electron-deficient alkenes.[6]

**Table I. Reaction of Complex 1 with Methyl Acrylate**



| entry | solvent | temp, °C | additive | yield of **6**, % | trans:cis **6** | yield of **7** |
|---|---|---|---|---|---|---|
| 1[a] | THF | 65 | none | 64 | 46:54 | 5 |
| 2 | THF | 65 | none | 63 | 48:52 | 9 |
| 3 | THF | 65 | $PPh_3$ | 39 | 26:74 | 7 |
| 4 | dioxane | 101 | none | 52 | 48:52 | 7 |
| 5 | dioxane | 101 | $PPh_3$ | 58 | 47:53 | 12 |

[a] Methyl acrylate was added to a refluxing solution of carbene complex 1 in THF.

If carbene complex **1** functions as a cyclopropanating reagent, donor–acceptor-substituted cyclopropanes (e.g., **5**) would be provided (Scheme II). The reaction of pentacarbonyl[phenyl(methoxy)methylene]chromium with electron-deficient alkenes leads to donor–acceptor-substituted cyclopropanes in good yields.[7] Donor–acceptor-

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