60 (24.8), 51 (5.5), and 50 (17.7).

Preparation of $CF_2ClC(O)CFHCOOEt$ (8l) (Method B). Yield: 2.8 g (67%). Bp: 60–65 °C (38 mmHg) (lit.[10] bp 162–164 °C (atm pressure)). GLPC purity 96%. ^{19}F NMR: see Table I. ^1H NMR: 5.6 (d, $^2J_{F,H_{gem}}$ = 48 Hz), 4.3 (q, $^3J_{H,H}$ = 7 Hz), and 1.4 (t). ^{13}C NMR: 206 (s), 166.3 (d, $^2J_{C,F}$ = 25 Hz), 128.1 (t, $^1J_{C,F}$ = 306 Hz), 88.2 (d, $^1J_{C,F}$ = 198 Hz), 62.2 (s), and 14.3 (s). IR: 2909 (w), 1763 (s), 1741 (s), 1200 (s), and 1028 (s). Mass spectrum: *m/e* 220 (2.8, $C_6H_6F_3O_3{}^{37}Cl$), 218 (11.5, $C_6H_6F_3O_3{}^{35}Cl$), 211 (13.3), 192 (11.8), 190 (35.5), 173 (10.6), 172 (14.4), 105 (100.0), 87 (40.8), 44 (10.4), and 40 (66.2).

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for financial support of this work.

Registry No. 1, 401-55-8; 8a, 1522-41-4; 8b, 759-67-1; 8c, 127224-01-5; 8d, 118460-47-2; 8e, 118460-46-1; 8f, 685-88-1; 8g, 1479-22-7; 8h, 127224-04-8; 8i, 127224-02-6; 8j, 127224-03-7; 8k, 685-69-8; 8l, 87405-76-3; 9, 2356-16-3; EtCOCl, 79-03-8; $(CH_3)_2CHCOCl$, 79-30-1; $(CH_3)_3CCOCl$, 3282-30-2; $C_6H_{11}COCl$, 2719-27-9; EtOCOCl, 541-41-3; PhCOCl, 98-88-4; $MeOCO(CH_2)_2COCl$, 1490-25-1; EtSCOCl, 2941-64-2; $F_3C(CF_2)_2COCl$, 375-16-6; F_3CCOCl, 354-32-5; $ClCF_2COCl$, 354-24-5; Bu_3P, 998-40-3; acetic anhydride, 108-24-7.

Supplementary Material Available: ^1H and ^{19}F NMR spectra for 8a–l (34 pages). Ordering information is given on any current masthead page.

Synthesis and Chemistry of a New, Functionalized Polycyclic Azoalkane. A Novel Entry into the Homopentaprismane Ring System

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Received May 10, 1990

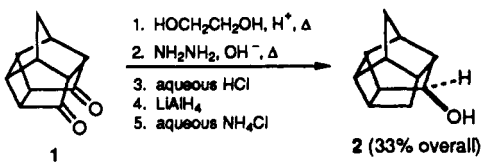
Reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione, **1**) with (*p*-tolylsulfonyl)hydrazine (1 equiv) followed by in situ reduction of the product thereby obtained with sodium borohydride afforded two products, i.e., hexacyclic azoalkane **3** (34%) and *exo*-3-(*p*-tolylsulfonyl)tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecan-*endo*-6-ol (**4**, 19%). The structure of **3** was established via X-ray crystallographic analysis of its corresponding *O*-benzoyl derivative **5a**. Reaction of **4** with acetic anhydride–pyridine gave the corresponding *O*-acetyl derivative **6**, whose structure was established by X-ray crystallographic methods. The corresponding reaction of **1** with (*p*-tolylsulfonyl)hydrazine alone afforded **3** as the exclusive reaction product in 66% yield. Subsequent reduction of **3** with sodium borohydride afforded **4** (84%). The results of mechanistic studies revealed that the conversion of **3** to **4** proceeds stepwise, i.e., with loss of nitrogen from **3** to form 3-(*p*-tolylsulfonyl)tetracylo[6.3.0.0^{4,11}.0^{5,9}]undec-2-en-6-one (**7**), which is subsequently reduced in situ by sodium borohydride. Irradiation of a benzene solution of **3** (Pyrex filter) afforded *exo*-(*p*-tolylsulfonyl)-PCUD-8-one (**9**, 48%). Similar irradiation of **5a** produced the corresponding substituted homopentaprismane (**11a**, 71%), whereas irradiation of **5c** (i.e., the *O*-acetyl derivative of **3**) gave a mixture of two products, i.e., homopentaprismane **11b** (52%) and the corresponding homohypostrophene **12** (14%), along with recovered **5c** (15%). The results of a control study revealed that **12** is not an intermediate in the formation of **11b** from **5c**. Structures of **9** and of **11a** were determined by X-ray crystallographic methods.

Introduction

As part of a general program that is concerned with the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCUDs),[1] we have recently undertaken the synthesis of some unusual cage amines via (i) reductive amination of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,11-dione (PCUD-8,11-dione, **1**)[2] and (ii) sodium borohydride and sodium cyanoborohydride reduction of PCUD-8,11-dione monobenzylimine.[3] Roughly spherical cage amines of this type are of interest as analogues of 1-aminoadamantane, whose activity as an antiviral and anti-Parkinsonism agent is well established.[4]

In this connection, it was of interest to prepare PCUD-*endo*-8-ol (**2**) in quantity as starting material for the synthesis of amino-substituted PCUDs. In the past, this compound has been prepared from **1** in four steps (Scheme I).[5] In the present study, a shorter alternative route was investigated wherein **2** might be synthsized in a one-pot, two-step process via (i) reaction of **1** with (*p*-tolylsulfonyl)hydrazine followed by (ii) in situ reduction of the corresponding PCUD-8,11-dione monotosylhydrazone thereby obtained with sodium borohydride.[6] However, in our hands, application of this reaction sequence starting with **1** failed to afford any of the desired product **2**. Instead, two other products, **3** and **4**, were obtained in 19% and 34% yield, respectively (Scheme II).

Scheme I



1 **2 (33% overall)**

Product Characterization. Structure characterization of **3** and **4** was accomplished in part via analysis of their

(1) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT; 1989; Vol. 1, pp 357–399.
(2) Marchand, A. P.; Dave, P. R.; Satyanarayana, N.; Arney, B. E., Jr. *J. Org. Chem.* **1988**, *53*, 1088.
(3) Marchand, A. P.; Arney, B. E., Jr.; Dave, P. R.; Watson, W. H.; Nagl, A. *J. Org. Chem.* **1988**, *53*, 2644.
(4) (a) Dekker, T. B.; Oliver, D. W. S. African Patent ZA 82 02,158 (to Noristan, Ltd.), 24 Dec. 1984, 52 pp; *Chem. Abstr.* **1986**, *104*, P148379s. (b) Weber, J. C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 5315.
(5) Dekker, T. G.; Oliver, D. W. *S. Afr. J. Chem.* **1979**, *32*, 45.
(6) (a) Caglioti, L. *Tetrahedron* **1966**, *22*, 487. (b) Caglioti, L. *Org. Synth.* **1972**, *52*, 122.

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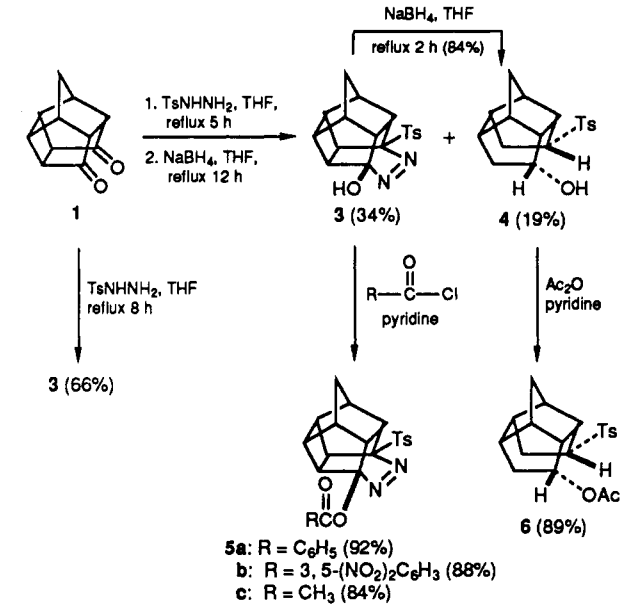
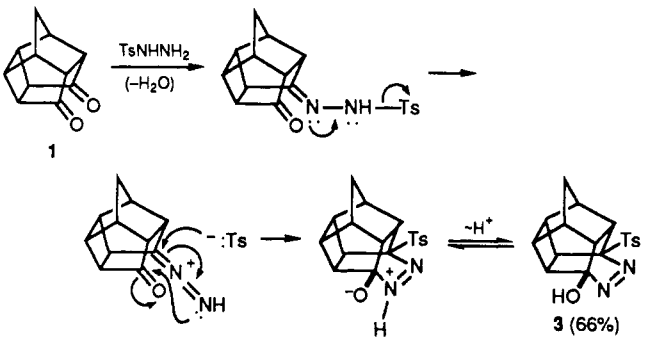
Scheme II



Scheme III



respective infrared (IR) and ^1H and ^{13}C NMR spectra. The IR spectra of both **3** and **4** displayed absorption at 3453 cm^{-1} (O–H stretching vibration). Their corresponding ^1H NMR spectra confirmed the presence of a *p*-tolylsulfonyl (Ts) moiety in each product, as indicated by singlets at δ 2.42 and at δ 2.41 (ArCH_3 groups in **3** and **4**, respectively) and by aromatic AB patterns (centered at δ 7.34 and 8.00 and at δ 7.30 and 7.76, respectively).

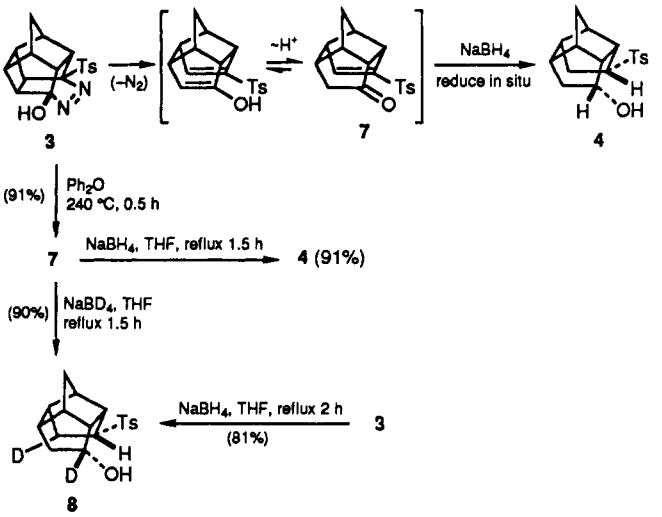
Unequivocal confirmation of the structure of **3** was obtained via single-crystal X-ray analysis of its corresponding *O*-benzoyl derivative **5a**. Similarly, X-ray structural analysis performed on the *O*-acetyl derivative of **4** (i.e., **6**) confirmed the structure of **4** (vide infra).

Mechanistic Studies. The reaction of **1** with (*p*-tolylsulfonyl)hydrazine alone was investigated in order to gain insight into the mechanism of formation of **3** and **4** in the two-step reaction sequence shown in Scheme II. Compound **3** was thereby obtained as the exclusive reaction product in 66% yield. One possible mechanism that accounts for the formation of **3** from **1** in this reaction is shown in Scheme III.

Subsequent reduction of **3** with sodium borohydride afforded **4** as the only reaction product in 84% yield. Thus, the intermediacy of **3** in the formation of **4** via sequential reaction of **1** with (*p*-tolylsulfonyl)hydrazine followed by reduction with sodium borohydride is strongly indicated.

We further suggest that the conversion of **3** to **4** proceeds in stepwise fashion, i.e., with loss of nitrogen from **3** to form enone **7** (Scheme IV) followed by in situ reduction of **7** by sodium borohydride to afford **3**. Evidence for this pathway

Scheme IV



was obtained in the following manner. The suggested intermediate **7** was synthesized independently via thermal decomposition of **3**. Subsequent reaction of **7** thereby obtained with sodium borohydride in refluxing THF afforded **4** in 91% yield. In addition, it was found that similar reaction of **7** with sodium borodeuteride followed by aqueous acidic workup afforded **8**, a specifically dideuterated analogue of **4**, in 90% yield. Finally, **8** could also be synthesized in 81% yield via direct reduction of **3** with sodium borodeuteride. These results are summarized in Scheme IV.

Sodium borohydride reduction of PCUD-8-one[5] and of substituted PCUD-8,11-diones[7] generally occurs from the exo face of the C=O double bond, thereby affording the corresponding endo alcohol. By way of contrast, the stereochemistry of the sodium borohydride reduction of **7** is unusual. Thus, whereas the ketone functionality in **7** is reduced, as expected, from the exo face, the corresponding reduction of the R_2C=CRTs moiety[8] in **7** is anomalous (i.e., the C(9)–Ts bond in the final product, **4**, is exo rather than endo).

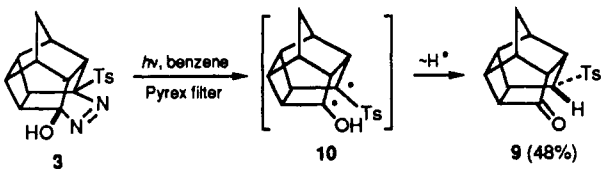
This result can be understood by assuming that reduction of the C=O group in **7** by sodium borohydride occurs faster than does the corresponding C=C bond reduction in this system. Inspection of molecular models reveals that there is insufficient room in the product, a substituted tetracyclo[6.3.0.$0^{3,7}$.$0^{4,11}$]undecane, to accommodate both an *endo*-6-OH and an *endo*-9-Ts functionality. If the C(9)–H bond in **4** is sufficiently acidic, equilibration might occur at C(9) under the reaction and/or workup conditions. The equilibrium would be expected to favor the observed product **4**, in which unfavorable endo,endo OH···Ts interaction is avoided.

Further evidence in this regard is provided by our observation that sodium borohydride reduction of **7** followed by workup with D_3O^+ affords **4** *without* concomitant incorporation of deuterium at C(9). Mechanistically, formation of a C(9)–D bond is expected in this reaction. The fact that repeated attempts at this reaction failed to afford monodeuterated **4** attests to the lability of the C(9)–D bond (which most likely suffers H–D exchange during the isolation and purification steps).

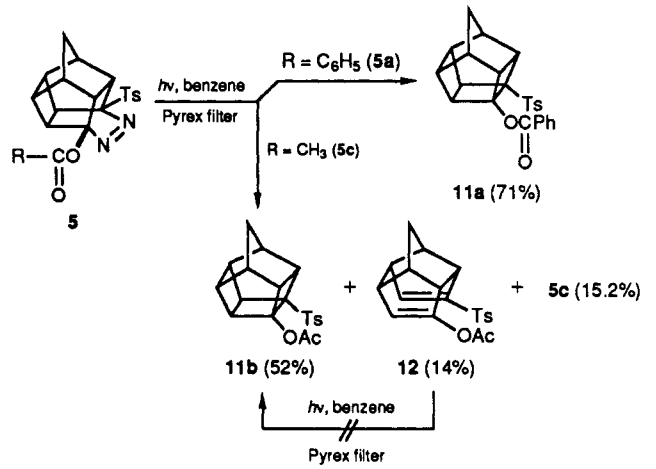
(7) Marchand, A. P.; LaRoe, W. D.; Sharma, G. V. M.; Suri, S. C.; Reddy, D. S. *J. Org. Chem.* **1986**, *51*, 1622 and references cited therein.

(8) Sodium borohyride reduction of thiete sulfone has been reported to result exclusively in reduction of the C=C double bond, thereby affording thietane sulfone. See: Dittmer, D. C.; Christy, M. E. *J. Am. Chem. Soc.* **1962**, *84*, 399.

Scheme V



Scheme VI

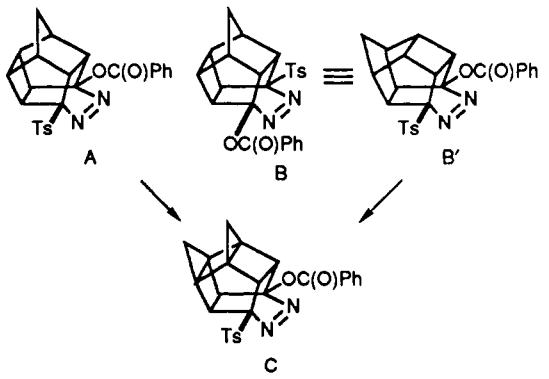


Photoreactions of 3, 5a, and 5c. Photochemical extrusion of nitrogen from polycyclic azoalkanes is of interest as a potential method for synthesizing cage hydrocarbon systems. Reactions of this type received considerable attention in recent years.[9] In this connection, we have examined the corresponding photodecompositions of azoalkanes **3**, **5a**, and **5c**.

Irradiation of a benzene solution of **3** under argon with a 450-W medium pressure mercury lamp (Pyrex filter) afforded pentacyclic ketone **9** (Scheme V). The structure of **9** was established unequivocally via single-crystal X-ray structural analysis (vide infra).

Dramatically different results were obtained when the corresponding *O*-benzoyl derivative **5a** was photolyzed under similar conditions. Thus, irradiation of a benzene solution of **5a** under argon with Pyrex-filtered light afforded the corresponding substituted homopentaprismane **11a** in 71% yield. By way of contrast, similar irradiation of the corresponding *O*-acetyl derivative **5c** afforded two products, i.e., the corresponding substituted homopentaprismane (**11b**, 52% yield) and a tetracyclic diene (**12**, 14% yield), along with recovered starting material (15.2% yield, see Scheme VI). The structure of **11a** was established unequivocally via single-crystal X-ray structural analysis (vide infra). Although the parent homopentaprismane and several of its derivatives have been synthesized,[10] **11a** is, to our knowledge, the first such compound to have been studied by direct methods.

Scheme VII



A control experiment established that **12** is not an intermediate when **11b** is formed via irradiation of **5c** in benzene with Pyrex-filtered light. Thus, **12** was synthesized independently by reacting **7** with isopropenyl acetate.[11] Irradiation of a benzene solution of **12** under argon with Pyrex-filtered light failed to afford any detectable trace of **11b**; only starting material and some unidentified decomposition products could be isolated from this reaction (see Experimental Section).

The foregoing observations indicate that two commonly occurring photoprocesses result when **3**, **5a**, and **5c** are irradiated with Pyrex-filtered light. (i) Loss of nitrogen occurs upon irradiation of **3**; the resulting 1,4-diradical **10** (Scheme V) subsequently undergoes radical–radical disproportionation with resulting intramolecular transfer of the hydroxylic hydrogen atom to the radical site adjacent to the *p*-tolylsulfonyl group, thereby affording **9**.[12] (ii) Similar irradiation of **5a** and **5c**, both of which lack a free hydroxyl group, follows a different course. Thus, in both instances, the major photoproduct (**11a** and **11b**, respectively) results via loss of nitrogen with concomitant formation of a new C(8)–C(11) σ bond. These might be concerted processes, or, alternatively, stepwise loss of nitrogen followed by cyclization of an intermediate 1,4-biradical might occur in either case.[13]

It was noted above that irradiation of **5c** afforded diene **12** as a minor reaction product in addition to **11b**. Again, **12** might result via either concerted or stepwise breakdown of **5c** with concomitant expulsion of nitrogen.[14] It is clear from the results of the control experiment that **12** does not lie on the reaction coordinate that leads from **5c** to **11b**.

X-ray Structures of 5a, 6, 9, and 11a. The two enantiomers of **5a** are depicted in Scheme VII). Crystal packing in **5a** is determined in large measure by requirements imposed by the tosyl and benzoyloxy side chains. Enantiomer B can be rotated in such a manner that the

(9) (a) See: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99 and references cited therein. (b) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108. (c) McElwee-White, L.; Dougherty, D. A. *Ibid.* **1985**, *107*, 4964. (d) Engel, P. S.; Keys, D. E.; Kitamura, A. *Ibid.* **1985**, *107*, 4964. (e) Adam, W.; Hannemann, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Wilson, R. M. *Ibid.* **1987**, *109*, 5250.

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(14) Fragmentation of the C(2)–C(3) σ bond in 1,4-diradicals, $^{\bullet}R_2C(1)-C(2)R_2-C(3)R_2-C(4)R_2^{\bullet}$, with concomitant formation of two alkene units has been observed frequently, particularly in systems where the C(2)–C(3) bond is contained within a strained ring. See: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99 and references cited therein.

(15) (a) Watson, W. H.; Nagl, A.; Marchand, A. P.; Reddy, G. M.; Reddy, S. P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *C45*, 659. (b) Watson, W. H.; Nagl, A.; Marchand, A. P.; Deshpande, M. N. *Ibid.* **1989**, *C45*, 1349.

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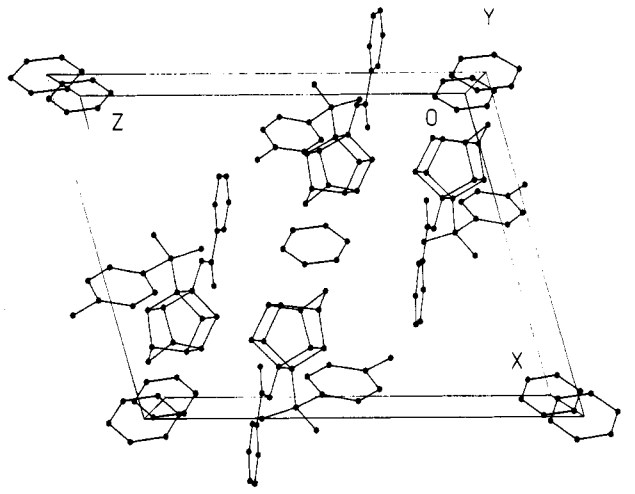

Figure 1. Crystal packing diagram of **11a**·(benzene).

tosyl, N=N, and benzoyloxy moieties in B can be superimposed upon the corresponding functionalities in enantiomer A (see structure B′ in Scheme VII). Superimposition of B′ upon A then results in a disordered structure, C, for **5a**. The two methylene bridges of the norbornyl moieties in A and B′ exhibit half occupancies. The atoms connected to the ends of the methylene bridges [i.e., C(2), C(4), C(1), and C(5)] do not exactly coincide when A and B′ are superimposed, but the resulting electron densities cannot be resolved into two peaks. This results in an average position for these atoms and a highly anisotropic thermal motion. Accordingly, bond distances and angles derived from X-ray data for **5a** that involve these carbon atoms are not reliable.

There are two independent molecules per triclinic cell of **6**, and sufficient data were obtained to permit their refinement. A brief discussion of bond lengths in **6** is given in the supplementary material.

Crystals obtained for **9** proved to be of poor quality. Thus, only limited data could be collected, and the bond distances and angles thereby obtained exhibit large standard deviations.

A structure drawing of **11a** is given in the supplementary material. Interestingly, the crystals of **11a** that we obtained contain benzene as a solvate molecule; a crystal packing diagram is shown in Figure 1. However, these crystals proved to be of poor quality, and some decomposition occurred during data collection. A brief discussion of bond lengths in **11a** is given in the supplementary material.

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, Lincoln, NE.

Stepwise Reaction of 1 with (*p*-Tolylsulfonyl)hydrazine ($TsNHNH_2$) and Sodium Borohydride. A solution of **1**[17] (1.74 g, 10 mmol) and $TsNHNH_2$ (1.86 g, 10 mmol) in tetrahydrofuran (THF, 40 mL) was refluxed for 5 h. The reaction mixture was allowed to cool to room temperature, and $NaBH_4$ (2.00 g, 52.6 mmol) was added portionwise with stirring. The resulting mixture was stirred at ambient temperature for 1 h and then heated to reflux. Reflux was maintained for 12 h, at which time the reaction mixture was allowed to cool to room temperature. The reaction mixture then was concentrated in vacuo, and ethyl acetate (120 mL) was added to the residue. The resulting mixture was washed successively with water (50 mL), 5% aqueous Na_2CO_3 (2 × 50 mL), 5% aqueous HCl (2 × 50 mL), and water (50 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by using a 20–35% ethyl acetate–hexane mixed solvent gradient elution scheme. The first chromatography fractions afforded **4** (610 mg, 19%) as a colorless microcrystalline solid: mp 126–129 °C; IR (KBr) 3453 (s), 2958 (s), 1600 (m), 1481 (m), 1309 (s), 1296 (s), 1279 (s), 1231 (m), 1155 (s), 1104 (s), 834 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.29–2.57 (complex m, 12 H, which contains CH_3 singlet at δ 2.41), 4.39–4.51 (m, 1 H), 5.02 (dd, J = 8.7 Hz, J' = 7.9 Hz, 1 H), 7.30 (*AB*, J_{AB} = 8.3 Hz, 2 H), 7.76 (*AB*, J_{AB} = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.38 (q), 28.10 (t), 31.14 (t), 33.78 (t), 40.41 (d), 43.01 (d), 44.10, (d), 46.01 (d), 47.18 (d), 48.44 (d),63.87 (d), 74.96 (d), 128.03 (d), 129.50 (d), 135.98 (s), 143.80; mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 163 (100.0), 145 (54.5).

Compound **4** was further characterized via its corresponding *O*-acetate, i.e., **6**, which was obtained in 89% yield via reaction of **4** with acetic anhydride in the presence of pyridine.[18] Compound **6** was thereby obtained as a colorless microcrystalline solid: mp 144–145 °C; IR (KBr) 2957 (s), 1773 (s), 1599 (m), 1320 (s), 1307 (s),1281 (s), 1253 (s), 1156 (s), 1105 (s), 1053 (s), 846 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.29–1.50 (m, 3 H), 1.89–2.55 (complex m, 15 H, which contains two CH_3 singlets at δ 1.95 and 2.41, respectively), 4.29–4.39 (m, 1 H), 5.04–5.16 (m, 1 H), 7.31 (*AB*, J_{AB} = 8.6 Hz, 2 H), 7.74 (*AB*, J_{AB} = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.10 (q), 21.54 (q), 27.93 (t), 31.17 (t), 31.56 (t), 39.94 (d), 43.38 (d), 44.16 (d), 45.77 (d), 46.94 (d), 47.29 (d), 65.14 (d), 76.79 (d), 128.28 (d), 129.72 (d), 136.20 (s), 144.27 (s), 170.15 (s). Anal. Calcd for $C_{20}H_{24}SO_4$: C, 66.65; H, 6.71. Found: C, 66.75; H, 6.72. An X-ray crystal structure was obtained for **6** (vide infra).

Further elution of the chromatography column afforded **3** (1.15 g, 34%) as a colorless microcrystalline solid: mp 200–202 °C dec; IR (KBr) 3453 (s), 2987 (m), 1601 (m), 1313 (s), 1163 (s), 1107 (m), 849 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.44 (*AB*, J_{AB} = 11.2 Hz, 1 H), 1.70 (*AB*, J_{AB} = 11.2 Hz, 1 H), 1.96–2.10 (m, 1 H), 2.19–2.33 (m, 2 H), 2.42 (s, 3 H), 2.50–3.26 (m, 6 H), 7.34 (*AB*, J_{AB} = 8.2 Hz, 2 H), 8.00 (*AB*, J_{AB} = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.61 (q), 37.43 (t), 39.99 (d), 42.39 (d), 43.09 (d), 43.68 (d), 44.12 (d), 45.73 (d), 47.02 (d), 51.55 (d), 98.89 (s), 105.75 (s), 129.46 (d), 130.43 (d), 132.93 (s), 145.27 (s).

Compound **3** resisted purification via recrystallization. We were unable to obtain material that melted over less than a ca. 2 °C range even after several recrystallizations from ethyl acetate–hexane and from chloroform–hexane. Accordingly, **3** was further characterized via the corresponding *O*-benzoyl derivative **5a**, which was obtained in 92% yield by reacting **3** with excess benzoyl chloride in the presence of pyridine.[18] Compound **5a** was thereby obtained as a colorless microcrystalline solid: mp 230–231 °C; IR (KBr) 2983 (m), 1715 (s), 1599 (m), 1324 (s), 1285 (s), 1251 (s), 1170 (s), 1135 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.48 (*AB*, J_{AB} = 10.5 Hz, 1 H), 1.76 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.40–2.54 (complex m, 4 H, which contains CH_3 singlet at δ 2.43), 2.70–3.35 (m, 7 H), 7.30–7.64 (m, 5 H), 7.97–8.14 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.68 (q), 37.54 (t), 39.79 (d), 42,12 (d), 42.29 (d), 43.56 (d), 43.60 (d), 45.73 (d), 46.78 (d), 49.94 (d), 98.28 (s), 110.13 (s), 128.47 (d), 129.56 (d), 129.86 (d), 130.18 (s), 130.79 (d), 132.99 (s), 133.47 (d), 145.42 (s), 165.19 (s). Anal. Calcd for $C_{25}H_{22}N_2O_4S$: C, 67.25; H, 4.97. Found: C, 67.22; H, 5.01. An X-ray crystal structure was obtained for **5a** (see supplementary material).

Compound **3** was further characterized via the corresponding *O*-3,5-dinitrobenzoyl derivative **5b**, which was obtained in 88% yield via reaction of **3** with excess 2,5-dinitrobenzoyl chloride in the presence of pyridine.[18] Compound **5b** was thereby obtained as a colorless microcrystalline solid: mp 228–229 °C; IR (KBr) 3087 (m), 2983 (m), 1731 (s), 1621 (m), 1599 (m), 1545 (s), 1466 (m), 1352 (s), 1284 (s), 1175 (s), 1096 (s), 940 (m), 845 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.51 (*AB*, J_{AB} = 11.4 Hz, 1 H), 1.79 (*AB*, J_{AB} = 11.4 Hz, 1 H), 2.40–2.52 (complex m, 4 H, which contains CH_3 singlet at δ 2.42), 2.72–3.36 (m, 7 H), 7.34 (*AB*, J_{AB} = 8.2 Hz, 2 H), 7.97 (*AB*, J_{AB} = 8.2 Hz, 2 H), 9.04–9.35 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.66 (q), 37.57 (t), 39.77 (d), 42.01 (d), 42.24 (d), 43.50

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(d), 43.58 (d), 45.64 (d), 46.86 (d), 49.93 (d), 98.27 (s), 112.08 (s), 122.79 (d), 129.52 (d), 129.61 (d), 130.62 (d), 132.64 (s), 133.68 (s), 145.63 (s), 148.66 (s), 161.21 (s). Anal. Calcd for $C_{25}H_{20}N_4O_8S$: C, 55.97; H, 3.75. Found: C, 56.24; H, 3.78.

Compound **3** was further characterized via the corresponding *O*-acetyl derivative **5c**, which was obtained in 84% yield via reaction of **3** with excess acetic anhyride in the presence of pyridine.[18] Recrystallization of the material thereby obtained from ethyl acetate–hexane mixed solvent afforded **5c** as a colorless microcrystalline solid: mp 108–109 °C; IR (KBr) 2986 (m), 1742 (s), 1327 (s), 1310 (s), 1239 (s), 1174 (s), 1141 (s), 1106 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.42 (*AB*, J_{AB} = 11.2 Hz, 1 H), 1.69 (*AB*, J_{AB} = 11.2 Hz, 1 H), 2.16 (s, 3 H), 2.30–2.62 (m, 2 H), 2.39 (s, 3 H), 2.67–3.35 (m, 6 H), 7.31 (*AB*, J_{AB} = 8.1 Hz, 2 H), 7.92 (*AB*, J_{AB} = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.39 (q), 21.66 (q), 37.22 (t), 39.35 (d), 41.77 (d), 41.95 (d), 43.22 (d, 2 C), 45.45 (d), 46.51 (d), 49.47 (d), 98.14 (s), 109.55 (s), 129.58 (d), 130.76 (d), 132.97 (s), 145.50 (s), 169.89 (s). Anal. Calcd for $C_{20}H_{20}N_2O_4S$: C, 62.49; H, 5.24. Found: C, 62.85, 62.69; H, 5.76, 5.70.

Reaction of 1 with $TsNHNH_2$ (1 equiv). A solution of **1** (1.74 g, 10 mmol) and $TsNHNH_2$ (1.86 g, 10 mmol) in THF (40 mL) was refluxed for 8 h. The reaction mixture was allowed to cool to room temperature and then was concentrated in vacuo. The residue was purified in the manner described above. Column chromatographic purification of the product afforded **3** (2.26 g, 66%): mp 200–202 °C. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of **3** that had been prepared previously by the method described above.

Sodium Borohydride Reduction of 3. To a solution of **3** (100 mg, 0.29 mmol) in dry THF (15 mL) was added $NaBH_4$ (100 mg, 2.6 mmol), and the resulting mixture was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature and then concentrated in vacuo. Water (10 mL) and 10% aqueous HCl (10 mL) were added sequentially to the residue, and the resulting mixture was extracted with methylene chloride (3 × 15 mL). The combined organic layers were washed with water (2 × 20 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by using 30% ethyl acetate–hexane mixed solvent as eluent. Compound **4** (78 mg, 84%) was thereby obtained as a colorless microcrystalline solid: mp 126–129 °C. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of **4** that had been prepared previously by the method described above.

Thermolysis of 3. A solution of **3** (250 mg, 0.73 mmol) in diphenyl ether (4 mL) was heated at 240 °C for 0.5 h. The crude reaction mixture was placed onto a silica gel chromatography column. Diphenyl ether was eluted with hexane. Further elution with 40% ethyl acetate–hexane mixed solvent afforded **7** (210 mg, 91%) as a colorless microcrystalline solid: mp 150–151 °C; IR (KBr) 2960 (s), 2883 (m), 1725 (s), 1596 (s), 1418 (m), 1323 (s), 1307 (s), 1163 (s), 1101 (s), 1035 (m), 874 (m), 838 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.65–2.30 (m, 4 H), 2.38–3.40 (complex multiplet, 12 H, which contains CH_3 singlet at δ 2.43), 6.71 (d, J = 3.9 Hz, 1 H), 7.31 (*AB*, J_{AB} = 8.2 Hz, 2 H), 7.73 (*AB*, J_{AB} = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.44 (q), 33.73 (t), 38.58 (d), 41.69 (t), 47.33 (d), 49.55 (d), 51.47 (d), 55.04 (d), 62.74 (d), 128.09 (d), 129.56 (d), 136.11 (s), 144.38 (s), 147.17 (d), 152.13 (s), 216.39 (s); mass spectrum (70 eV), *m/e* (relative intensity) 314 (molecular ion, 100.0), 175 (39.7), 159 (65.3), 139 (49.6). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found: C, 69.16; H, 5.81.

Sodium Borohydride Reduction of 7. To a solution of **7** (40 mg, 0.13 mmol) in dry THF (10 mL) under nitrogen was added with stirring $NaBH_4$ (40 mg, 1.0 mmol), and the resulting mixture was refluxed for 1.5 h. The reaction mixture was allowed to cool to room temperature and then concentrated in vacuo. Water (20 mL) was added to the residue, and the resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with water (2 × 15 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo. Compound **4** (37 mg, 91%) was thereby obtained as a colorless microcrystalline solid: mp 126–129 °C. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of **4** that had been prepared previously (vide supra).

The *O*-acetyl derivative of this material was prepared in 88% yield by reacting it with excess acetic anhydride in the presence of pyridine.[18] The material thereby obtained displayed mp 144–145 °C; this melting point was undepressed upon admixture with authentic **6**, synthesized previously (vide supra).

Sodium Borodeuteride Reduction of 7 (H_2O Workup). To a solution of **7** (46 mg, 0.15 mmol) in dry THF (10 mL) was added under argon with stirring $NaBD_4$ (40 mg, 0.95 mmol), and the resulting mixture was refluxed for 1.5 h. The reaction mixture was allowed to cool to room temperature and then concentrated in vacuo. Water (25 mL) was added to the residue, and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (2 × 20 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo. Compound **8** (42 mg, 90%) was thereby obtained as a colorless microcrystalline solid: mp 113–118 °C; IR (KBr) 2143 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.15–2.72 (complex m, 15 H, which contains CH_3 singlet at δ 2.39), 5.0 (d, J = 8.7 Hz, 1 H), 7.31 (*AB*, J_{AB} = 8.7 Hz, 2 H), 7.77 (*AB*, J_{AB} = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.35 (q), 27.79 (t, J_{CD} = 19.2 Hz), 31.14 (t), 33.64 (t), 40.42 (d), 42.99 (d), 44.06 (d), 46.08 (d), 47.27 (d), 48.44 (d), 63.90 (d), 74.85 (t, J_{CD} = 22.0 Hz), 128.33 (d), 129.76 (d), 136.36 (s), 144.10 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 165 (100.0), 147 (33.1).

Sodium Borodeuteride Reduction of 3 (H_2O Workup). To a solution of **3** (50 mg, 0.15 mmol) in dry THF (10 mL) was added under argon with stirring $NaBD_4$ (50 mg, 1.2 mmol), and the resulting mixture was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature and then was concentrated in vacuo. Water (20 mL) was added to the residue, and the resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with water (2 × 15 mL), dried (Na_2SO_4), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by using 20% ethyl acetate–hexane mixed solvent as eluent. Compound **8** (41 mg, 81%) was thereby obtained as a colorless microcrystalline solid: mp 113–118 °C. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of **8** that had been prepared previously via $NaBH_4$ reduction of **7** (vide supra).

Photolysis of 3. A solution of **3** (250 mg, 0.73 mmol) in benzene (250 mL) under argon was irradiated with a 450-W medium pressure mercury lamp (Pyrex filter) for 12 h. The reaction mixture was concentrated in vacuo, and the residue was purified via chromatography on silica gel by using 20% ethyl acetate–hexane mixed solvent as eluent. Compound **9** (110 mg, 48%) was thereby obtained as a colorless microcrystalline solid: mp 174–175 °C; IR (KBr) 2993 (s), 1728 (s), 1599 (m), 1327 (s), 1302 (s), 1289 (s), 1263 (m), 1164 (s), 1105 (s), 845 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.62 (*AB*, J_{AB} = 11.2 Hz, 1 H), 1.84 (*AB*, J_{AB} = 11.2 Hz, 1 H), 2.39 (s, 3 H), 2.48–3.30 (m, 9 H), 7.30 (*AB*, J_{AB} = 7.8 Hz, 2 H), 7.60 (*AB*, J_{AB} = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.47 (q), 36.75 (d), 37.62 (t), 38.75 (d), 42.20 (d), 43.50 (d), 43.97 (d), 46.92 (d), 48.51 (d), 52.56 (d), 67.86 (d), 128.14 (d), 129.83 (d), 135.19 (s), 144.80 (s), 216.74 (s); mass spectrum (70 eV), *m/e* (relative intensity) 314 (molecular ion, 4.1), 159 (100), 131 (50.1). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found: C, 69.08; H, 5.79.

Photolysis of 5a. A solution of **5a** (120 mg, 2.69 mmol) in benzene (250 mL) under argon was irradiated with a 450-W medium pressure mercury lamp (Pyrex filter) for 1.5 h. The reaction mixture was concentrated in vacuo, and the residue was purified via chromatography on silica gel by using 20% ethyl acetate–hexane mixed solvent as eluent. Compound **11a** (80 mg, 71%) was thereby obtained as a colorless microcrystalline solid: mp 199–200 °C; IR (KBr) 2978 (m), 1711 (s), 1312 (s), 1299 (s), 1284 (s), 1270 (s), 1243 (s), 1179 (s), 1127 (s), 1112 (s), 765 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.49 (*AB*, J_{AB} = 10.7 Hz, 1 H), 1.61 (*AB*, J_{AB} = 10.7 Hz, 1 H), 2.33 (s, 3 H), 2.57–3.58 (m, 8 H), 7.18–7.57 (m, 5 H), 7.80 (*AB*, J_{AB} = 8.1 Hz, 2 H), 8.01 (*AB*, J_{AB} = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.37 (q), 40.19 (t), 42.47 (d), 46.85 (d), 47.45 (d), 48.34 (d), 48.71 (d), 49.33 (d), 50.48 (d), 52.86 (d), 75.58 (s), 91.30 (s), 128.57 (d), 128.60 (d), 129.38 (s), 129.75 (d), 129.85 (d), 133.50 (d), 135.45 (s), 144.64 (s), 164.87 (s). Anal. Calcd for $C_{25}H_{22}O_4S$: C, 71.75; H, 5.30. Found: C, 72.10; H, 5.30.

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); ^{1}H NMR ($CDCl_3$) δ 1.54 (*AB*, J_{AB} = 12.0 Hz, 1 H), 1.62 (*AB*, 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 (*AB*, J_{AB} = 7.9 Hz, 2 H), 7.24 (*AB*, J_{AB} = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 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); ^{1}H NMR ($CDCl_3$) δ 1.61 (*AB*, J_{AB} = 10.7 Hz, 1 H), 1.70 (*AB*, 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 (*AB*, J_{AB} = 8.2 Hz, 2 H), 7.80 (*AB*, J_{AB} = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 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, ^{1}H 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 ^{1}H 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.

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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