Comparative Study of *syn*- and *anti*-1,5-Bishomocycloheptatrien-2-yl Radicals and Carbocations

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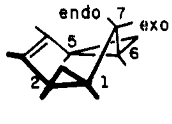
syn-1,5-Bishomocycloheptatriene (1) was found to undergo free-radical halogenation (*t*-BuOCl, *hν*) at one of its two equivalent allylic cyclopropyl positions to give unrearranged chloride **5**. Further treatment of **5** with this reagent led to symmetrical dichloride **6**. The conversion of *anti*-1,5-bishomocycloheptatriene (**2**) to **7** proceeded analogously, but **7** proved to be stable to the reaction conditions. Methanolysis of **5** and **7** in neat methanol at 100–150 °C or with silver trifluoroacetate catalysis at room temperature proceeded with opening of the functionalized three-membered ring to give ethers **10–12**. The regioselectivity of free radical hydrogen abstraction and the retention of structural integrity during the formation of **5** and **7** are contrasted with the chemical response obtained during conversion of these chlorides to their carbocations.

Hydrocarbons **1** and **2**, synthesized recently for the purpose of assessing long-range cyclopropyl interaction and σ homoaromaticity,[2–5] incorporate an interesting spectrum of unique structural features. For example, the conformationally rigid **1**, where both cyclopropyl groups adopt the thermodynamically favored extended "equatorial" arrangement, constrains H_2 and H_5 to lie in plane with the $p\pi$ orbitals located on C_3 and C_4 and projects $H_{7\text{-endo}}$ into a bisected ralationship with *both* three-membered rings. In anti isomer **2a**, H_5 remains well aligned with the C_3–C_4 π bond, but H_2 is now almost orthogonal to that plane. Also, while $H_{7\text{-endo}}$ bisects the 5,6-fused cyclopropane ring, $H_{7\text{-exo}}$ is oriented properly for maximum interaction with the "axial" three-membered ring positioned at C_1,C_2. However, since **2a** is in mobile degenerate equilibrium with **2b** at room temperature (E_a = 8.13 kcal/mol)[2] and these pairs of hydrogens experience rapid time averaging under such conditions, all four can presumably attain a chemical environment capable of substantially enhancing their chemical reactivity.



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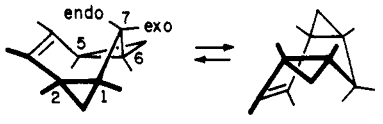
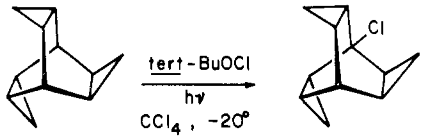


2a 2b

Those forms of possible conjugative interaction available to **1** and **2** are therefore: (a) *allylic*, but with requisite abstraction of a cyclopropyl hydrogen (H_2 or H_5 in **1**, H_5 in **2a**, or H_2 in **2b**) to achieve delocalization; (b) *biscyclopropylcarbinyl* ($H_{7\text{-endo}}$ in **1** only); and (c) *cyclopropylcarbinyl* ($H_{7\text{-endo}}$ or $H_{7\text{-exo}}$ in **2**). In an effort to determine the extent to which these extrasymmetric factors affect the regioselectivity of free-radical attack, **1** and **2** have been subjected to chlorination with *tert*-butyl hypochlorite. Strikingly specific abstraction of H_2 or H_5 has been observed in both examples with formation of structurally unrearranged chlorides. This paper concerns an analysis of this unprecedented selectivity and contrasts the structural integrity of the intermediate bishomocycloheptatrienyl free radicals to the lability of their carbocationic counterparts.

Chlorination Experiments. Upon reaction of simple hydrocarbons with elemental chlorine in the gas phase, a reactivity order for hydrogen abstraction of tertiary > secondary > primary is generally seen, but the quite low selectivity (maximum range of 5–6)[6] usually leads to production of complex mixtures.[7] Low-level C–H bond elongation at the transition state has consequently been implicated,[8] although various degrees of looseness in the activated complex seemingly can become operational as hydrocarbon structure is altered.[9] The incorporation of cyclopropane rings into the molecular framework contributes to enhanced selectivity, especially favoring the cyclopropylcarbinyl site. Thus, while Walling and Fredricks established that cyclopropane itself has 1/20 the reactivity of a normal secondary hydrogen toward Cl· at 0 °C,[10] Roberts and Mazur showed that methylcyclopropane undergoes photochlorination predominantly via methyl hydrogen abstraction to give chloromethylcyclopropane and 4-chloro-1-butene.[12]

With more highly strained molecules such as bicyclo[2.1.0]pentane[14] and nortricyclene,[15] chlorine prefers to enter into polar addition reactions. Olefinic substrates share this common problem. For abstraction of allylic hydrogens, the reagent of choice is *tert*-butyl hypochlorite, since *tert*-butoxy radical addition to double bonds does not prevail. Walling's extensive examination of the reactions of *t*-BuOCl with a variety of olefins has shown that an allylic hydrogen is activated with respect to a corresponding saturated hydrogen atom.[16] More recent work by de Meijere's group has established that the cyclopropylcarbinyl sites in trishomobarrelene (**3**) and trishomobullvalene (**4**) are specifically halogenated by this reagent.[17] Further, Schallner has demonstrated the utility of fluorotrichloromethane (Freon 11) as a low-temperature solvent for such photochlorinations.[18]



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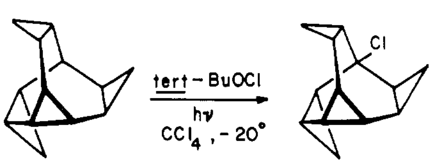

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Irradiation of a cold (−63 °C) solution of **1** and *tert*-butyl hypochlorite in Freon 11 for 45 min provided a single monochloride (**5**) and a dichloride (**6**) as major products (85%), together with several more extensively halogenated materials which were not further investigated. Preparative VPC purification gave **5** and **6** in 46 and 6% isolated yields, respectively. When **5** was resubmitted to the conditions of chlorination, efficient conversion to **6** (71% isolated) was realized. Since the ^{13}C NMR spectrum of **5** consists of nine lines arising from one quaternary, five tertiary (including the two olefinic centers), and three secondary carbon atoms, substitution clearly had not occurred at a biscyclopropylcarbinyl site (C_7), a cyclopropyl methylene position, or the double bond (C_3, C_4).

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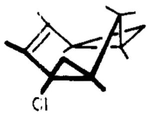
Comparable analysis of **6** revealed this dichloride to be a symmetrical molecule. Off-resonance decoupling established the five signals to arise from two quaternary, four tertiary, and three secondary sites. These data are uniquely consistent with radical substitution at C_1,C_6 or C_2,C_5 in the bishomotropilidene.



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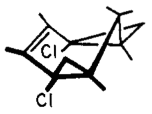
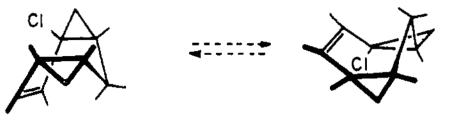


6

A clean distinction between these possibilities can be made by analysis of the ^1H NMR spectra. In $CDCl_3$, $H_{7\text{-exo}}$ and $H_{7\text{-endo}}$ of hydrocarbon **1** appear at δ 2.47 and 0.32 as a doublet of multiplets (J = 14 Hz) and a multiplet, respectively. This rather characteristic pattern is unaltered in **5** (δ 2.53 and 0.80) and somewhat more sharply structured in **6** [δ 2.60 (d of t, J = 14 and 5.5 Hz) and 0.07 (d of t, J = 14 and 11 Hz)]. Therefore, only long-range or virtual H–H coupling is affected upon chlorination. The protons adjacent to C_7 must consequently have remained intact. That chlorination had occurred at C_2 and C_5 is further revealed by the reduced level of spin–spin interaction operating on the cyclopropyl methylene protons relative to **1**.

With these assignments of structure, it is immediately obvious that the allylic cyclopropane hydrogens in **1** are most reactive. Furthermore, halogenative substitution has occurred without structural rearrangement, in line with the preestablished reluctance of cyclopropyl radicals to relieve strain through ring opening.[19]

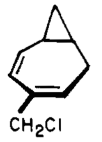
Submission of **2** to analogous reaction with *tert*-butyl hypochlorite gave 62% of a colorless oil composed predominantly (85%) of monochloride **7**. Although attempts to purify **7** by VPC and column chromatographic techniques usually led to rearrangement (see below), ^{13}C NMR analysis of a carefully purified sample (see Experimental Section) showed clearly that substitution had again taken place at a tertiary allylic cyclopropyl site (see Experimental Section). The ^1H NMR spectrum shows the protons bonded to C_7 to be widely separated (multiplets at δ 2.50 and 1.40), but does not provide indication whether the favored conformer is **7a** or **7b**. The olefinic protons of the chloride appear as a multiplet centered at δ 5.70, at slightly lower field than in **2**. The two cyclopropyl methylene protons which are projected over the seven-membered ring have moved to higher field, with that presumed to be on the chlorinated ring appearing at δ 1.05 and the other at δ 0.70. The remaining hydrogens resonate in the region δ 1.50–1.10.



7a 7b

Molecule **7a** is so structured that the chlorine atom occupies a pseudoequatorial position, while in **7b** the halogen is projected in a pseudoaxial direction and normally should be less favored for the usual energetic reasons. For mechanistic reasons, **7b** must be the initial product of free-radical substitution. Since **7** is not subject to further chlorination as is **5**, this may mean that conformer **7a** (where H_2 is now properly stereoaligned with the π bond) is not present in reasonable quantities at low temperatures. The inference would be that **7b** is highly populated under these conditions. However, since the argument rests on negative evidence, this conclusion is obviously tenuous.

Rearrangement Reactions. To achieve purposeful rearrangement of **7** under purely thermal conditions, the neat chloride was sealed in a glass ampule and immersed in an oil bath heated at 150 °C for 4 h. ^1H NMR analysis of the product indicated that complete rearrangement to **8** had occurred. Similar results could be achieved upon passing **7** through VPC columns heated to 180 °C or more efficiently by elution through Florisil with hexane (100% yield). Structural assignment to **8** follows from mass spectral, combustion, ultraviolet, and NMR evidence. For example, its electronic spectrum (in cyclohexane) is characterized by a single maximum at 232 nm (ϵ 3100) as expected for such a homotropilidene.[20] In the NMR spectrum, the olefinic protons appear as a doublet of doublets (J = 5 and 11 Hz) at δ 6.22 (1 H) and a multiplet centered at δ 5.70 (2 H). Additionally, the $-CH_2Cl$ protons are seen as a broadened singlet at δ 3.87, downfield of the allylic cycloheptyl methylene multiplet at δ 2.43–1.97. This pattern, as well as that exhibited by the cyclopropyl hydrogens, is generally characteristic of this class of dienes and particularly **9**.[21]



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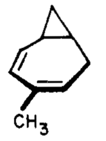

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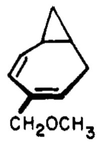

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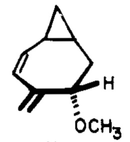

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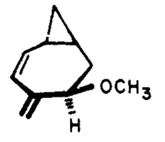
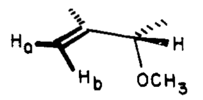


12

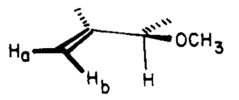
The greater solvolytic reactivity of **7** as compared to **5** was made evident through experiments conducted in anhydrous methanol. Upon heating **7** in this solvent at 100 °C (sealed tube) for 4 h, conversion to a mixture of **10** (94%), **11** (4%), and **12** (2%) was observed; **5** remained unresponsive and could be recovered. However, at 150 °C **5** was transformed to **10** (95%), **11** (4%), and **12** (1%) after 4 h.

Treatment of either chloride with a slight excess of silver trifluoroacetate in methanol at room temperature for brief periods of time led to the same three methyl ethers, although in somewhat different ratios (for **5**, 73.5, 7, and 19.5%; for **7**, 67.5, 15, and 17.5%).

In the case of **10**, its structure follows directly from its ultraviolet and ^1H NMR spectra. With the exception of the methyl signal shown by **9** and the methoxylmethyl peaks exhibited by **10**, their spectra are otherwise essentially superimposable. The proton spectra of **11** and **12** clearly define their gross structural features. To distinguish between the epimers, recourse to molecular models was made. For **13**, the preferred conformation appears to be that which places the methoxyl substituent below the plane defined by the exo methylene group. In the geometry given by A, the magnetic environments of the terminal olefinic protons become rather similar and could reasonably correspond to the broadened singlet absorption (2 H) shown by **11** a δ 5.03. For **12**, the same ring conformation appears again to be favored, thereby necessitating that the methoxyl group approach syn proton H_b rather closely (see B). Operation of a through-space shielding effect would be expected to cause H_b to appear at lower field than



A



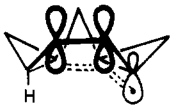
B

H_a. In fact, ether **12** shows H_b and H_a to be widely divergent in their chemical shifts. These protons appear as multiplets centered at δ 5.27 and 4.97, respectively. Although this basis for stereochemical assignment is not totally unequivocal, it does appear entirely reasonable.

Independent treatment of **8** with silver trifluoroacetate in methanol afforded **10**, **11**, and **12** in the ratio 55:20.5:24.5. Since **10** proved to be stable to these reaction conditions, ethers **11** and **12** must be primary products in all the rearrangements examined in this study.

Discussion

An interesting feature of the free-radical chlorination of bishomocycloheptatrienes **1** and **2** is the regioselectivity of abstraction favoring an allylic cyclopropyl hydrogen. The observed reactivity is viewed as the combined result of structurally enforced geometry which fixes H_2 or H_5 in plane with the $p\pi$ orbitals and the resonance stabilization available to free radicals **13** and **14**. The customary bond strength and higher electronegativity of a cyclopropyl C–H bond is thereby effectively lowered to the point where other possible reactions are hardly competitive. This reasoning assumes that the transition states leading to **13** and **14** resemble products more than starting materials. In this way, the activated complexes can profit energetically from their proximity to the potential minima on the reaction profile.



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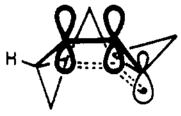
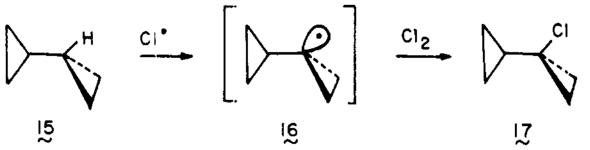


14

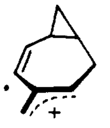
The formation of tertiary chlorides **5** and **7** without structural rearrangement parallels earlier discoveries which have shown that cyclopropyl radicals normally fail to ring open. The closest analogy known to us is the vapor-phase chlorination of bicyclopropyl (**15**) which proceeds via cyclopropylcarbinyl-stabilized radical **16** to **17** with retained structural integrity.[22]



15 16 17

In contrast to the stability of **13** and **14**, the cyclopropane ring comprising the seat of reaction during carbocation generation does not remain structurally intact. Since the product compositions obtained from direct methanolysis of these chlorides are identical, the intervention of a common intermediate satisfactorily represented by allyl cation **18** is implicated. The differences in the ratios of ethers **10–12** obtained in the Ag^+-assisted reactions are considered to arise because of somewhat earlier transition states where less structural reorganization has had time to occur. The isomeric differences between **13** and **14** consequently become more apparent.

Qualitatively speaking, the solvolytic behavior of **5** and **7** is somewhat enhanced relative to that of simpler cyclopropyl halides.[22-24] Chloride **7**, which necessarily must have one of its cyclopropane rings axially disposed, is the more reactive as a consequence of its higher ground-state energy. The products of methanolysis are consistent with electrocyclic ring opening concerted with ionization,[25] as found previously for 1-vinylcyclopropyl tosylate.[26] Significantly, disrotatory ring fission synchronous with departure of the leaving group would necessitate that only low-level positive change density actually develop on the originally functionalized carbon,[27] such charge distribution precluding the possibility of efficient vertical stabilization[28] by the adjoining vinyl group as in **19**. Evidently, any stabilization which might accrue to **19** is inadequate to impede the facile ring opening giving rise to **18** which releases inherent strain while likely occurring with little or no energy barrier.[27,29]



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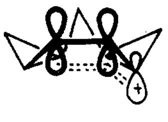

19

In summary, the preceding results reveal that the π bond of a vinylcyclopropane can activate an allylic cyclopropyl hydrogen to free-radical substitution but cannot reduce the barrier to (conrotatory?)[30] ring opening of the three-membered ring despite the possible release of $\sim$30 kcal/mol of energy.[31] When cations are involved, essentially the reverse chemical response is seen. Cyclopropyl ring fission concurrent with ionization presumably obtains while delocalization of positive charge by comparable vertical stabilization is not of primary importance.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments and apparent splittings are given in all cases. The ^{13}C spectra were also run on the Bruker spectrometer. Mass spectra were measured with an AEI-MS9 spectrometer at an ionization energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2-Chloro-*syn*-1,5-bishomocycloheptatriene (5) and 2,5-Dichloro-*syn*-1,5-bishomocycloheptatriene (6). A solution of 1[2] (300 mg, 2.5 mmol) and *tert*-butyl hypochlorite (400 mg, 36 mmol) in 3 mL of Freon 11 contained in a 10-mm Pyrex NMR tube was placed in a chloroform–liquid nitrogen slush bath (−63 °C) contained in a Pyrex Dewar flask. The reaction mixture was irradiated for 45 min with a Sylvania sunlamp, diluted with 15 mL of ether, washed with saturated sodium bicarbonate solution, and dried. Concentration and preparative VPC purification showed two products (ratio 85:15) to dominate the mixture (85%). The more rapidly eluted major component (176 mg, 46%) was a colorless oil identified as monochloride **5**: IR ν_{max} (neat) 3070, 3000, 2920, 2860, 1650, 1450, 1130, 825, and 725 cm^{-1}; ^{1}H NMR δ_{Me_4Si} (CCl_4) 5.62 (s, 2), 2.53 (d of t, J = 13 and 4 Hz, 1), 2.08–1.03 (br m, 4), 0.80 (d of t, J = 7 and 4 Hz, 1), 0.50 (t, J = 5.5 Hz, 1), and 0.00 (m, 2); ^{13}C NMR ($CDCl_3$) 131.4 (d), 128.9 (d), 41.2 (s), 34.3 (k), 28.7 (d), 25.1 (t), 15.0 (d), 14.2 (t), and 12.8 ppm (d); *m/e* calcd 154.0549, found 154.00554.

Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17. Found: C, 69.74; H, 7.22.

The second component proved to be dichloride **6**: ^{1}H NMR δ_{Me_4Si} (CCl_4) 5.82 (s, 2), 2.60 (d of t, J = 14 and 5.5 Hz, 1), 1.92 (m, 2), 1.30 (d of d, J = 9 and 5 Hz, 2), 0.58 (t, J = 5 Hz, 2), and 0.07 (d of t, J = 14 and 11 Hz, 1); ^{13}C NMR ($CDCl_3$) 130.1 (d), 39.4 (s), 34.9 (t), 28.6 (d), and 25.1 ppm (t); *m/e* 188.

Chlorination of 5. A solution of **5** (20 mg, 0.13 mmol) and *tert*-butyl hypochlorite (17 mg, 0.16 mmol) in 0.4 mL of Freon 11 was irradiated as described above for 45 min. The reaction mixture was diluted with ether (10 mL), washed with saturated sodium bicarbonate solution, dried, and concentrated to give 17 mg (71%) of **6**, identical in all respects with the above sample.

2-Chloro-*anti*-1,5-bishomocycloheptatriene (7). A solution of **2**[2] (240 mg, 2.00 mmol) and *tert*-butyl hypochloride (220 mg, 2.04 mmol) in 2 mL of Freon 11 was allowed to react as described previously. Molecular distillation [65 °C (0.2 Torr)] afforded 119 mg (62%) of a colorless oil, VPC analysis of which showed it to be composed chiefly (86%) of one component. Preparative VPC purification under carefully controlled conditions (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 120 °C) gave pure **7**: IR ν_{max} (neat) 3020, 2920, 1645, 1450, 1123, 1037, 810, and 785 cm^{-1}; ^{1}H NMR δ_{Me_4Si} (CCl_4) 5.70 (m, 2), 2.50 (br m, 1), 1.40 (br m, 1), 1.50–1.10 (m, 5), 1.05 (m, 1), and 0.70 (m, 1); ^{13}C NMR ($CDCl_3$) 130.6 (d), 126.5 (d), 41.8 (s), 27.2 (t), 25.3

(d), 24.1 (t), 16.9 (d), 14.5 (d), and 12.8 ppm (t); *m/e* calcd 154.0549, found 154.0554.

Anal. Calcd for $C_{911}Cl$: C, 69.90; H, 7.17. Found: C, 69.74; H, 7.33.

4-Chloromethylbicyclo[5.1.0]octa-2,4-diene (8). A. Thermal Rearrangement of 7. A small sample of chloride **7** was sealed neat in a small glass ampule which was immersed in an oil bath preheated to 150 °C. After 4 h, the ampule was opened and the residual liquid was examined by ^{1}H NMR. The spectrum was identical with that of **8** as prepared on a preparative scale below.

B. Florisil-Promoted Rearrangement of 7. Chloride **7** (50 mg, 0.32 mmol) was adsorbed onto 2 g of activated Florisil using hexane as solvent. After 15 min, the product was eluted with hexane to give 50 mg (100%) of **8**; ^{1}H NMR δ_{Me_4Si} (CCl_4) 6.22 (d of d, J = 11 and 5 Hz, 1), 6.00–5.40 (m, 2), 3.87 (br s, 2), 2.43–1.97 (m, 2), 1.80–0.70 (m, 3), and 0.43 (d of t, J = 9 and 3 Hz, 1); UV λ_{max} (cyclohexane) 232 nm (ϵ 3100); *m/e* calcd 154.0549, found 154.0552.

Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17. Found: C, 69.48; H, 7.11.

Methanolysis Experiments. A. Silver(I)-Assisted Ionization. To a 0.1 M solution of **5** or **7** in anhydrous methanol (purified by distillation from magnesium methoxide) was added 1.1–1.2 equiv of silver trifluoroacetate (Aldrich). The resulting mixture was allowed to stir at room temperature for 1–4 h. After filtration and dilution with water, the products were extracted into petroleum ether and the combined organic layers were washed with brine, dried, and concentrated. Product analysis, accomplished by VPC methods on a 10 ft × 0.25 in. 15% XF-1150 column (Chromosorb P, 120 °C), revealed conversion to a mixture of ethers **10**, **11**, and **12**. The individual components were purified by preparative scale separation (for **5**, 73.5, 7, and 19.5%; for **7**, 67.5, 15, and 17.5%).

For **10**: IR ν_{max} (neat) 3000, 2920, 2880, 2830, 2810, 1610, 1440, and 1090 cm^{-1}; UV λ_{max} (cyclohexane) 251 nm (ϵ 2900); ^{1}H NMR δ_{Me_4Si} (CCl_4) 6.23 (d of d, J = 11.5 and 4.5 Hz, 1), 5.75 (m, 1), 5.60 (d, J = 11.5 Hz, 1), 3.82 (br s, 2), 3.29 (s, 3), 2.60–2.20 (m, 2), 1.63 (m, 1), 1.40–0.80 (m, 2), and 0.80–0.30 (m, 1); *m/e* calcd 150.1045, found 150.1048.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.83; H, 9.56.

For **11**: ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 5.80 (m, 2), 5.03 (s, 2), 3.80 (d, J = 8 Hz, 1), 3.34 (s, 3), 2.61 (m, 1), 1.70–0.80 (m, 4), and 0.15 (m, 1); *m/e* calcd 150.1045, found 150.1048.

For **12**: ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 5.83 (s, 1), 5.80 (br s, 1), 5.27 (m, 1), 4.98 (m, 1), 3.93 (m, 1), 3.43 (s, 3), 2.47 (m, 1), 1.70–0.70 (m, 4), and 0.20 (m, 1); *m/e* calcd 150.1045, found 150.1048.

Comparable treatment of **8** afforded 56% of **10**, 24% of **11**, and 20% of **12**.

B. Uncatalyzed Solvolyses. A solution of **7** (25 mg) in 2 mL of purified methanol was sealed in a glass ampule and heated in an oil bath at 100 °C for 4 h. The contents of the ampule were concentrated in vacuo and analyzed on the XF-1150 column: 94% of **10**, 4% of **11**, and 2% of **12**.

Comparable reaction of **5** but at 150 °C gave an identical distribution of the three ethers.

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