the photochlorination of 0.48 M DMB in 6.88 M c-C_6H_{12} (Table III), the procedure involved the addition of a solution of Cl_2 in CCl_4 (0.20 mL) to argon-purged cyclohexane (0.80 mL) containing DMB (0.066 mL), followed by reaction and GC analysis. The photochlorination of neat DMB was carried out by bubbling 7% Cl_2–N_2 through argon-purged DMB (2 mL) for a short time (2–30 s) in the dark, sealing the tube and then allowing the reaction to proceed to completion in the presence of light. In all these systems, the initial concentration of chlorine was calculated from the measured total yields of monochlorides. The data presented in Tables II and III have been corrected to allow for the 2-ClDMB that was formed by reaction of $Cl_3C^\bullet$ radicals with DMB.

The photochlorination of thoroughly degassed DMB was accomplished in the following way. Neat DMB (10 or 50 mL), together with a glass-coated magnet were introduced into a Pyrex reaction vessel containing a break-seal. The DMB was degassed on a high-vacuum line by six freeze–thaw cycles and sealed under vacuum. Chlorine gas was measured (manometer with no exposed mercury) and sealed into a 1.0-mL tube separated from the DMB by the glass break-seal. This was then broken (in the dark), and the resulting Cl_2/DMB solution was stirred to ensure homogeneity. The photochlorination and analysis were carried out in the usual way. The yield of DMB chlorides agreed, within experimental error, with the calculated amount of chlorine added.

Relative Reactivities of DMB and Cyclohexane toward the Trichloromethyl Radical. *n*-Decanoyl peroxide (20 mg, 0.058 mmol) was dissolved in a deoxygenated mixture of DMB (0.25 mL, 1.92 mmol), cyclohexane (0.25 mL, 2.30 mmol), and carbon tetrachloride (0.50 mL). The solution was maintained at 40 °C for 17 days and was then analyzed by GC. From the relative yields of DMB monochlorides and cyclohexyl chloride, the relative reactivity of the two alkanes toward $Cl_3C^\bullet$ was calculated. The selectivity for the DMB chlorination, under these conditions, was also measured.[25]

EPR Measurements. Deoxygenated solutions of DMB (0.40 mL) containing *n*-pentanoyl peroxide (30 μL) were photolyzed in the cavity of a Varian E104 EPR spectrometer with a 1000-W high-pressure mercury lamp. Relative concentrations of *n*-butyl and tertiary DMB radicals were determined by manual double integration of appropriate lines in the first-derivative EPR spectrum. Absolute radical concentrations were calibrated against DPPH,[42] with all measurements being made in the same tube.

Gas-Phase Chlorination. A 1-L reaction bulb on a specially constructed vacuum line (no greased stopcocks, no exposed mercury) was evacuated and filled with DMB vapor at 30 Torr. A small quantity (ca. 1 Torr) of Cl_2 was delivered to this bulb from a reservoir at 100 Torr. The reaction bulb was irradiated for 48 h, and the products were then condensed and subjected to GC analysis.

Acknowledgment. We thank Professor G. A. Russell for some extremely helpful comments that led us to initiate the present work.

Registry No. DMB, 79-29-8; 2-DMB$^\bullet$, 24436-98-4; CCl_4, 56-23-5; c-C_6H_{12}, 110-82-7; $Cl_3C^\bullet$, 3170-80-7; $(CH_3CH_2CH_2CH_2CO_2)_2$, 925-19-9; $CH_3CH_2CH_2CH_2^\bullet$, 2492-36-6.

Supplementary Material Available: Derivation of the integrated rate expression, I (2 pages). Ordering information is given on any current masthead page.

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β-Scission of 8-Hydrindanoxyl and Related Free Radicals

Dale E. O'Dell, John T. Loper, and Timothy L. Macdonald*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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The β-scission of alkoxyl free radicals prepared from thermolysis (77 °C) of the in situ generated hypoiodite derived from structurally related hydrindan-8-ol and hydrinden-8-ol systems was examined. The course of alkoxyl radical β-scission was sensitive to changes in alkyl substitution at the ring junction site and olefin introduction in the hydrindan skeleton. Thus, the cleavage pattern must reflect the interplay of multiple thermodynamic and kinetic factors.

Alkoxyl free radicals undergo a variety of synthetically useful intramolecular hydrogen abstraction and β-scission processes. We have been examining the potential of β-scission reactions of alkoxyl free radicals, situated at ring fusion sites, for the synthesis of medium- and large-ring systems via selective carbon–carbon bond cleavage.[1] Our initial studies on the course of alkoxyl radical β-scission in 9-decalinoxyl and several structurally related free radicals demonstrated that the mode of alkoxyl fragmentation in these systems is highly sensitive to changes in the molecular geometry of the precursor alcohol. The mode of β-scission in unsymmetrical alkoxyl free radicals[2,3] has been rationalized by considerations of the relative stabilities of the resultant carbon-centered free radical and carbonyl[4] or cyclic ketone components,[5] by analysis of stereoelectronic factors,[6] and by frontier molecular orbital theory.[7]

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(2) For reviews of alkoxy radical β-scission, see: (a) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (b) Brun, P.; Waegell, B. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, pp 367. (c) Kochi, J. K. *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, p 665. (d) Minisei, F.; Citterio, A. *Advances in Free Radical Chemistry*; Williams, C. H., Ed.; Heyden: London, 1980; Vol. 6, p 128.

(3) For recent examples of alkoxyl radical fragmentation processes, see: (a) Suginome, H.; Senboku, H.; Yamada, S. *Tetrahedron Lett.* **1988**, *29*, 79. (b) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. (c) Kobayashi, K.; Itoh, M.; Suginome, H. *Tetrahedron Lett.* **1987**, *29*, 3369. (d) Decorzant, R.; Vial, C.; Naf, F.; Whitesides, G. M. *Tetrahedron* **1987**, *43*, 1871. (e) Suginome, H.; Itoh, M.; Kobayashi, K. *Chem. Lett.* **1987**, 1527. (f) Schreiber, S. L.; Sammakia, T.; Hulin, B.; Schulte, G. *J. Am. Chem. Soc.* **1986**, *108*, 2106. (g) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2116. (h) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 8102. (i) Schreiber, S. L.; Liew, W. F. *J. Am. Chem. Soc.* **1985**, *107*, 2980.
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(5) (a) Majerski, Z.; Janjatovic, J. *Tetrahedron Lett.* **1979**, 3977. (b) Janjatovic, J.; Majerski, Z. *J. Org. Chem.* **1980**, *45*, 4892.
(6) (a) Brun, P.; Waegell, B. *Tetrahedron* **1976**, *32*, 517. (b) Bensadoun, N. I.; Brun, P.; Casanova, J.; Waegell, B. *J. Chem. Res., Synop.* **1981**, 236 and references therein.
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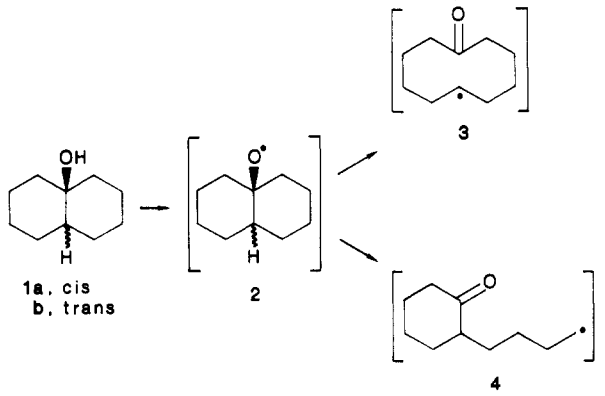
However, none of these factors was solely responsible for the direction of fragmentation in the examples that we have studied.[1]

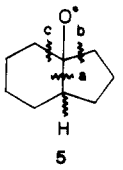
Insight into the factors associated with the fragmentation of *cis*- and *trans*-9-decalinoxyl radicals was provided by Beckwith et al.[8] These researchers found that in the β-scission of 9-decalinoxyl radicals **2**, generated in situ from hypobromite photolysis or thermolysis, fission of the 9–10 bond to generate cyclodecanone radical **3** is rapid and reversible, but fission of the 1–9 bond to butylcyclohexanone radical **4** is relatively slow and essentially irreversible. Thus, product formation from the fragmentation



of 9-decalinols **1** is highly dependent upon reaction conditions; at low temperatures (0 °C) in the presence of suitable radical traps, products derived from cyclodecanone radical **3** are predominantly produced, whereas at higher temperatures (81 °C), products are almost exclusively produced from butylcyclohexanone radical **4**.[8] Thus, both kinetic and thermodynamic factors play roles in the outcome of these β-scission reactions. We report here on the β-scission of alkoxyl free radicals prepared from thermolysis (at 77 °C) of the in situ generated hypoiodite derived from several structurally related 8-hydrindanol systems.

Results and Discussion

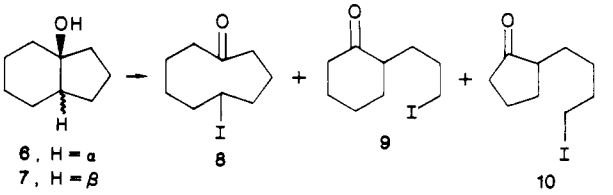
We undertook studies on the β-scission of hydrindanoxyl and related free radicals in order to augment our earlier studies of this process in decalinoxyl systems[1] and to further elucidate the factors responsible for the directionality of carbon–carbon bond fragmentation in cyclic alkoxyl radicals. The hydrindanoxyl radical system **5** has available three fragmentation pathways. On the basis of



5

studies by Greene[4] and Walling,[9] the cleavage of a cyclopentane ring was anticipated to be more favorable than cleavage of the cyclohexane ring in the fused hydrindan skeleton. Moreover, since β-scission reactions of tertiary alkoxy radicals normally produce products generated from the most stable radical intermediates,[2,4,8,9] we anticipated that the ring fusion bond (pathway a in **5**) would be the most susceptible bond to breakage. As in our previous studies, we employed mercuric oxide/iodine[10] in refluxing carbon tetrachloride (77 °C) as the reagents for the in situ formation of hypoiodites and their thermally initiated fragmentation. In order to obtain satisfactory yields in cleavage reactions with these sensitive alcohols, a solution of iodine in carbon tetrachloride was added slowly to a mixture of mercuric oxide and tertiary alcohol in carbon tetrachloride at reflux; if iodine was present in significant excess, dehydration of the tertiary alcohol occurred rapidly.

Treatment of *cis*-8-hydrindanol (**6**) with the conditions for in situ hypohalite formation and fragmentation gave three products determined to be 5-iodocyclononanone (**8**) (36%), 2-(3-iodopropyl)cyclohexanone (**9**) (15%), and 2-(4-iodobutyl)cyclopentanone (**10**) (18%). We next turned



our attention toward examining the impact of ring fusion stereochemistry on the mode of fragmentation. *trans*-Hydrindan systems with a substituent in a ring fusion site (typically) possess greater strain energy than their analogous *cis*-hydrindan systems, due to increased gauche interactions.[12] However, treatment of *trans*-8-hydrindanol (**7**)[11] provided the same three products [**8** (16%), **9** (17%), and **10** (10%)], in slightly different percentages than those derived from the cis analogue **6**. The related, although not identical, ratios of products from both the *cis*- and *trans*-8-hydrindanol ring systems suggest that the strain of the precursor hypohalite does not play a determining role in these β-scission processes. As in the decalinoxyl system, rapid equilibration between the fragmentation and reannealing of the *cis*- and *trans*-hydrindanoxyl radicals (**5**) may occur.[8,13] Thus, the observed product ratio may arise as a consequence of differences in the rates for ring opening and closure of the intermediate radical species with iodine.

Alkyl substitution at ring junction sites has a significant impact on the direction of β-scission and on the yields of isolated products in the hydrindanol system. Since tertiary centers undergo β-scission much more effectively (~300 times faster)[2,9] than primary free radicals in acyclic fragmentation processes, we anticipated that 9-methyl-8-hydrindanol (**11**) would produce products derived principally from the tertiary radical cleavage mode (pathway a in **5**). Upon treatment of methylhydrindanol **11** with the in situ hypoiodite generation–cleavage conditions, a sole product was isolated (22%) and tentatively identified as 2-iodo-6-methyl-6(*Z*)-cyclononenone (**12**). It is unlikely that β-scission to generate either primary alkyl radical occurs to a significant extent in these reactions.[14] How-

(8) Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718.

(9) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(10) For previous studies with this reagent, see the following and references therein: (a) Takahashi, H.; Ho, M.; Suginome, H.; Masamune, T. *Chem. Lett.* **1979**, 901. (b) Aktar, M.; Marsh, S. *J. Chem. Soc. C* **1966**, 937.

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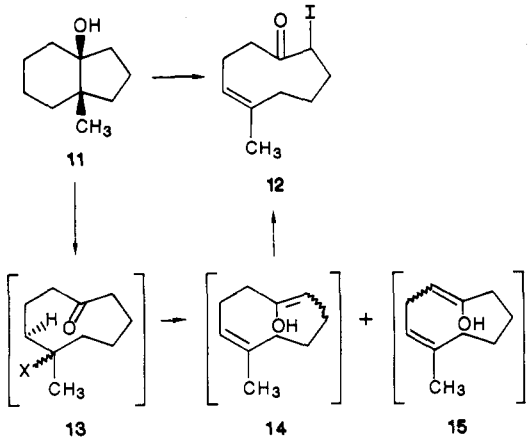
(13) For additional examples of alkoxyl radical epimerization, see: (a) Binkley, R. W.; Kohlic, D. J. *J. Org. Chem.* **1979**, *44*, 2047. (b) Nickon, A.; Ferguson, R.; Bosch, A.; Iwadare, T. *J. Am. Chem. Soc.* **1977**, *99*, 4518.

(14) This statement is based on the observation that the primary iodide fragmentation products typically possess reasonable stability to the β-scission reaction conditions and thus can generally be isolated if produced. For example, the following primary fragmentation products could be recovered (>85%) after resubmission to the reaction conditions: 2-(3-iodopropyl)cyclohexanone (**9**), 6-(3-iodopropyl)-6-methyl-2-cyclohexenone (**17**), 2-(4-iodobutyl)cyclohexanone,[1] and 6-(4-iodobutyl)-6-methyl-2-cyclohexenone.[1]

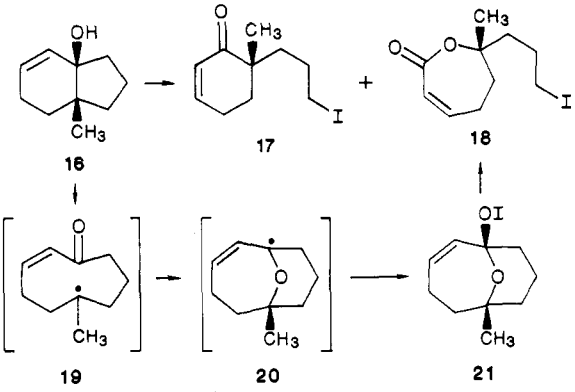


ever, the production of a single isolated product may not reflect a highly regioselective series of fragmentation–hydrogen iodide elimination–enolization–iodination reactions, due to the low yield of isolated product (which could be a consequence of selective destruction of alternate products) and to nature of the reaction conditions (which could affect both olefin geometry and position isomerization, as well as halide isomerization of the α-halo ketone moiety). A possible mechanistic pathway for the formation of the unsaturated α-iodo ketone involves internal carbonyl-induced elimination (of the tertiary iodide, carbocation, or radical) followed by (possibly regioselective) enolization and iodination of the derived enol isomer by a positive iodine source (iodine or iodine oxide generated in situ from mercuric oxide/iodine) [e.g., 11 → 13 (X = I, +, ·) → 14 → 12]. In this context it is interesting to note that the energy difference between enols 14 and 15 is approximately 1 kcal/mol (based on calculations of the minimum energy conformations of enols 14 and 15) by MM II calculation.

Our structure assignment of iodo ketone 12 is based on spectral considerations. Analysis of the ^1H NMR, ^{13}C NMR, and infrared spectra indicated that a *Z*-vinyl methyl substituent[15] and an α-iodo ketone moiety were present in the product. Of the four a priori possible isomers of 5-vinylic methyl substituted α-iodo-(*Z*)-cyclononenone, only structure 12 satisfies the spectral data.

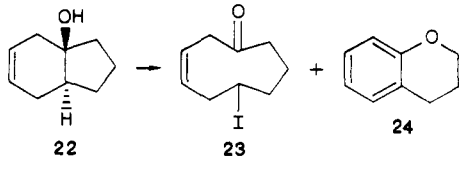
We then turned our attention to exploring the effects of olefin introduction in the 8-hydrindanol nucleus on the mode of ring cleavage. We had previously demonstrated that the introduction of unsaturation into the bicyclo[4.4.0] decalinol framework had a substantial influence on the course of ring cleavage. For example, *trans*-2-octalin-9-ol generated exclusively 5-(4-iodobutyl)-3-cyclohexenone (77% yield), and *cis*- and *trans*-10-methyl-1-octalin-9-ol generated exclusively 5-(4-iodobutyl)-5-methyl-2-cyclohexenone (95% and 91% yields, respectively).[1] These results are remarkable in that the fragmentation processes in these unsaturated systems do not take advantage of the substantial stabilization afforded the intermediate radical by either allylic resonance or tertiary substitution.

The impact of unsaturation on the mode of thermally induced alkoxyl radical β-scission is further illustrated in the hydrinden-8-ol series. Thus, 9-methyl-1-hydrinden-8-ol (16) was found to undergo fragmentation generating exclusively medium-ring products (17 and 18), whereas the saturated counterpart (11) undergoes cleavage to produce exclusively large-ring products (12). Under our in situ generation–fragmentation conditions, β-scission of hydrindenol 16 provided enone 17 (45% yield) and lactone 18



(37% yield). Although enone 17 presumably arises from initial fragmentation of the primary cyclopentyl-fused bond in hydrindenol 16, lactone 18 must arise from a more complex series of reactions. We postulate that initial cleavage of the ring fusion bond (to 19) is followed by intramolecular trapping by the carbonyl oxygen to give an allyloxy free radical (20), which is then trapped by hypoiodite (–OI) to produce an intermediate hypoiodite (21). The derived hypoiodite 21 subsequently undergoes homolytic cleavage to generate the observed lactone 18. Consistent with this proposed scheme is the observation that exposure of 6-(3-iodopropyl)-6-methylcyclohex-2-enone (17) to the reaction conditions does not result in the formation of lactone 18 (<5% by ^1H NMR analysis of the unpurified reaction mixture). Thus, as in the saturated case (11), the expected tertiary radical (19) is formed. However, due to factors inherent in the molecule, intramolecular carbonyl oxygen trapping occurs rather than intermolecular iodine trapping or dehydrogenation. In addition, a related mechanism was invoked by Suginome et al.[16] to explain the formation of an iodo formate produced in the transformation of a cyclic alcohol into a cyclic ether.

Hydrindenol 22 offers the opportunity to further differentiate between thermodynamic considerations of radical product stability and stereoelectronic concerns associated with the near orthogonality of the π-framework and the allylic carbon–carbon bond. Upon submission of hydrindenol 22 to the in situ hypoiodite generation–fragmentation conditions, only products (23 and 24) arising from cleavage of the fused cyclopentane ring were isolated.



However, the potential exists for selective decomposition under the reaction conditions of 2-(iodobutenyl)cyclopentanone derived from the allylic radical via cyclohexenyl bond cleavage. Iodo enone 23 is presumably derived from initial fragmentation of the ring fusion bond and subsequent iodine trapping. In contrast, chroman (24) must be generated from a more complex series of reactions. Presumably this sequence of reactions is initiated by cyclopentane ring opening to produce the primary radical, which then undergoes internal O-trapping (of either the radical or derived iodide) to engender an intermediate dihydrochroman. Subsequent iodine-mediated aromatization of the dihydrochroman species then provides the product

(15) See, for example: Marfat, A.; McQuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888.

(16) (a) Suginome, H.; Yamada, S. *J. Org. Chem.* **1984**, *49*, 3753. (b) Suginome, H.; Yamada, S.; Miyaura, N. *Chem. Lett.* **1983**, 55.

(24). A related sequence was observed in the fragmentation processes of the decalinol series.[1] Whatever the precise mechanisms associated with the generation of products from these hydrindanol or hydrindenol substrates, the predominant modes of fragmentation tend to involve cyclopentane ring cleavage.

These studies demonstrate that, as in our previous studies of decalinoxyl radical cleavage, the course of alkoxyl radical β-scission in these hydrindanyl systems must reflect the interplay of multiple factors. If the principles elucidated by Beckwith et al.[8] for 9-decalinoxyl radicals prove to be general for the β-scission of cyclic alkoxyl radicals, then the molecular features of the alcohol substrate may play a greater role in defining the rate constants for fragmentation and internal re-addition than in dictating the directionality of ring opening due to stereoelectronic considerations or to fragmentation adduct or resultant carbonyl stabilities. Thus, differing modes of fragmentation could be expected in these systems as a function of reaction conditions, the "kinetically irreversible" product being formed under the thermally induced hypohalite decomposition conditions employed in these studies, and the "kinetically preferred" product being formed via low-temperature, photolytically initiated hypohalite fragmentation. The ability to direct the alkoxyl cleavage pathway through reaction condition selection would significantly augment the synthetic potential of these reactions. However, at present, the precise nature or impact of these factors remains undetermined, and a priori predictions concerning the mode of β-scission in these cyclic systems are tenuous.

Experimental Section

General Procedures. Proton magnetic resonance spectra were recorded at 100 MHz with a JEOL JNM-MH-100 spectrometer, employing tetramethylsilane as an internal standard. ^{13}C magnetic resonance spectra were recorded at 22.50 MHz, by employing a JEOL FX-90Q Fourier-transform spectrometer with deuteriochloroform (77.0 ppm) as internal standard. Low-resolution mass spectra were obtained by direct insertion with an LKB 9000 spectrometer at 70 eV. Infrared spectra were obtained on a Perkin-Elmer 727 infrared spectrometer or a Perkin-Elmer 621 grating infrared spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. For column chromatography, E. Merck (type 60) silica gel or Florisil (100 mesh) and short-column techniques were utilized, and for TLC analysis, E. Merck silica gel 60, F-254 precoated (0.25 mm) plates were employed. Calcium chloride and magnesium sulfate were used as drying agents throughout, and all experimental procedures were performed under an atmosphere of dry nitrogen. All reported yields represent chromatographically isolated materials. The tertiary carbinols employed in this study were either known (**6**,[11] **7**,[11] and **22**[11a]) or synthesized via a short sequence (**11** and **16**). All substrates were subjected to identical β-scission reaction conditions. A representative experimental procedure for β-scission follows.

General Procedure for β-Scission Reactions.[1] A solution of iodine (0.330 g, 1.30 mmol) in carbon tetrachloride (30 mL) was added slowly (1 h) to a refluxing solution of the tertiary carbinol (0.65 mmol) in carbon tetrachloride (15 mL) containing yellow mercuric oxide (0.280 g, 1.32 mmol). The solution was refluxed (1 h), cooled, filtered, and then extracted twice with a saturated aqueous solution of sodium metabisulfite (50 mL) and once with brine (50 mL). The organic layer was dried and filtered, and the solvent was removed in vacuo to afford the crude product. In order to obtain product isomer yields, we chromatographed the residue (Florisil) and characterized the isolated products.

β-Scission of *trans*-Octahydro-3a*H*-inden-3a-ol (6).[11] *trans*-Octahydro-3a*H*-inden-3a-ol (**6**) (0.091 g, 0.65 mmol) was treated by the general procedure for β-scission to yield, after Florisil chromatography [EtOAc (5%)/petroleum ether (95%)], 5-iodocyclononanone (**8**) (0.062 g, 36%), 2-(3-iodopropyl)cyclohexanone (**9**) (0.027 g, 15%), and 2-(4-iodobutyl)cyclopentanone (**10**) (0.031 g, 18%). 5-Iodocyclononanone (**8**) was isolated as a light brown oil having the following spectral characteristics: ^1H NMR ($CDCl_3$, Me_4Si) δ 4.36 (quintet, J = 6 Hz, 1 H), 2.2–2.6 (br m, 6 H) 1.4–2.2 (br m, 8 H); IR (neat) (cm^{-1}) 2950 (s), 1705 (s), 760 (m); ^{13}C NMR ($CDCl_3$) 216.39, 43.31, 42.06, 38.32, 34.69, 34.26, 26.40, 24.45, 23.37 ppm; MS, m/e (relative intensity) 266 (4), 151 (41), 139 (47), 121 (59), 109 (100).

The carbocyclic parent structure of **8** was confirmed by its reduction (n-Bu_3SnH, benzene, AIBN) to cyclononanone. The structures of **9** and **10** were confirmed by independent synthesis (NaI/acetone displacement of the corresponding bromides).[17]

β-Scission of *cis*-Octahydro-3a*H*-inden-3a-ol (7).[11] *cis*-Octahydro-3a*H*-inden-3a-ol (**7**) (0.091 g, 0.65 mmol) was treated in identical fashion to yield 5-iodocyclononanone (**8**) (0.028 g, 16%), 2-(3-iodopropyl)cyclohexanone (**9**) (0.026 g, 15%), and 2-(4-iodobutyl)cyclopentanone (**10**) (0.019 g, 11%).

Synthesis of *cis*-Octahydro-7a-methyl-3a*H*-inden-3a-ol (11) and *cis*-1,2,3,6,7,7a-Hexahydro-7a-methyl-3a*H*-inden-3a-ol (16).[18] **1. 3a,4,7,7a-Tetrahydro-7a-methyl-3a,4-epoxy-5(6*H*)-indanone (28)** was prepared by employing a procedure developed by Trost and Salzmann[19] for the synthesis of epoxy derivatives of hydrindenones.

Lithium aluminum hydride (0.135 g, 5.62 mmol) was added cautiously to a solution of 7,7a-dihydro-7a-methyl-5(6*H*)-indanone (**25**)[20] (0.500 g, 3.60 mmol) in anhydrous ether (25 mL) cooled to 0 °C. The reaction mixture was stirred for 30 min and then quenched by the addition of water (2 drops), 10% NaOH (2 drops), and water (7 drops) sequentially, then petroleum ether (50 mL) was added, and the slurry was stirred for 30 min. The granular precipitate was removed by filtration through a plug of glass wool, and the residue was washed with petroleum ether (25 mL). The solvent was removed in vacuo to yield allyl alcohol **26** (0.474 g, 95%) as a thick clear oil. A solution of *m*-chloroperoxybenzoic acid (0.80 g, 4.0 mmol) in methylene chloride (25 mL) was added dropwise over 1 h to a solution of allyl alcohol **26** (0.525 g, 3.51 mmol) in methylene chloride (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for an additional 30 min and then quenched by aqueous base extraction (two times with 5% w/w aqueous NaOH and once with brine). The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to yield cis-fused epoxy alcohol **27** (0.501 g, 90%) as a thick clear oil. Epoxy alcohol **27** (0.529 g, 32.2 mmol) and sodium acetate (0.110 g, 1.33 mmol) were dissolved in methylene chloride (20 mL), and pyridinium chlorochromate (1.10 g, 5.05 mmol) was added in small portions while the solution was stirred with a mechanical stirrer. The reaction mixture was stirred for 3 h at room temperature, then quenched by the addition of ether (80 mL), and vacuum filtered through a Florisil column. The Florisil column was washed with ether (80 mL) and the solvent removed from the filtrate in vacuo to yield epoxy ketone **28** (0.464 g, 87%) as

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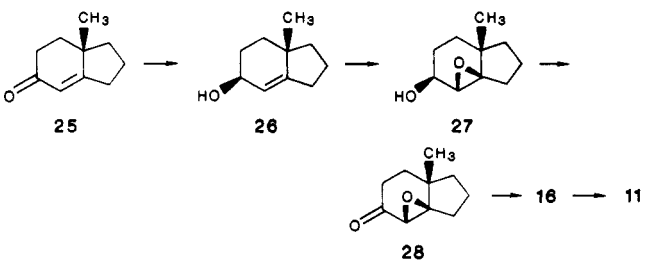
(18) These 9-methyl-8-hydrindan(en)ol fragmentation precursors were synthesized via the following short scheme. All attempts to synthesize epoxy ketone **28** (or *epi*-**28**) using basic hydrogen peroxide or *tert*-butyl hydroperoxide treatment of enone **25** failed. For similar results and an alternate approach after which the following scheme was patterned, see ref 19.



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a clear thick oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.12 (s, 1 H), 2.75 (dd, J = 8 Hz, 3 Hz, 1 H), 1.5–2.3 (br m, 9 H), 1.25 (s, 3 H); IR (neat) (cm^{-1}) 2960, 2860, 1725, 1715, 1460, 1400, 1370, 1180, 890, 870, 850; ^{13}C NMR ($CDCl_3$) 208.31, 78.46, 60.91, 40.76, 38.86, 37.07, 32.52, 31.01, 21.47, 21.15 ppm; MS, m/e (relative abundance) 166 (18), 138 (61), 110 (80), 83 (100). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.05; H, 8.40.

2. *cis*-1,2,3,6,7,7a-Hexahydro-7a-methyl-3a*H*-inden-3a-ol (16). Adopting the procedure of Wharton and Hohlen[21] for the synthesis of similar tertiary allyl alcohols, we added glacial acetic acid (2 drops, catalytic amount) to a solution of 3a,4,7,7a-tetrahydro-7a-methyl-3a,4-epoxy-5(6*H*)-indanone (**28**) (0.300 g, 1.79 mmol) in hydrazine hydrate (0.290 g, 5.37 mmol) at room temperature. Rapid bubbling occurred upon addition, and the solution became orange in color. After 1 h, water (50 mL) was added and the aqueous layer was extracted with diethyl ether (three times, 50 mL). The organic layers were combined, dried ($MgSO_4$), and filtered, and the solvent was removed in vacuo to yield *cis*-1,2,3,6,7,7a-hexahydro-7a-methyl-3a*H*-inden-3a-ol (**16**) as a yellow oil. Column chromatography [SiO_2; EtOAc (10%)/petroleum ether (90%)] of the crude product gave **16** as a clear oil (0.110 g, 40%): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.78 (s, 2 H), 1.2–2.2 (m, 10 H), 1.04 (s, 3 H); IR (neat) (cm^{-1}) 3400 (s), 2960 (s), 1440 (m), 1055 (s); ^{13}C NMR ($CDCl_3$) 153.02, 127.38, 79.82, 42.87, 38.81, 36.04, 31.71, 22.39, 21.53, 19.25 ppm; MS, m/e (relative abundance) 152 (50), 134 (100). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.24; H, 10.80.

3. *cis*-Octahydro-7a-methyl-3a*H*-inden-3a-ol (11). A Parr flask (250 mL) was charged with 10% Pd/C (50 mg), ethyl acetate (25 mL), and *cis*-1,2,3,6,7,7a-hexahydro-7a-methyl-3a*H*-inden-3a-ol (**16**) (0.200 g, 1.23 mmol). The flask was attached to an atmospheric hydrogenation apparatus and evacuated via an aspirator, H_2 was introduced, the flask was evacuated, and H_2 was reintroduced. The mixture was stirred for 3 h, resulting in the uptake of 30 mL of H_2. The flask was removed, the solution filtered, and the solvent removed in vacuo. The residue was chromatographed (SiO_2, 10% EtOAc in petroleum ether) to yield *cis*-octahydro-7a-methyl-3a*H*-inden-3a-ol (**11**) (0.186 g, 92%) as a white solid (mp 35 °C): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.2–2.2 (m, 15 H), 1.02 (s, 3 H); IR (neat) (cm^{-1}) 3450 (s), 2950 (s), 1470 (m), 1050 (m), 970 (m); ^{13}C NMR ($CDCl_3$) 81.39, 44.17, 37.62, 35.83, 35.61, 33.50, 23.64, 21.74, 19.68, 18.27 ppm; MS, m/e (relative abundance) 154 (100), 136 (50). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.74; H, 11.67.

β-Scission of *cis*-Octahydro-7a-methyl-3a*H*-inden-3a-ol (11). *cis*-Octahydro-7a-methyl-3a*H*-inden-3a-ol (**11**) (0.100 g, 0.651 mmol) was treated with the general procedure for β-scission to yield 2-iodo-6-methyl-6(*Z*)-cyclononenone (**12**) (43.0 mg, 22%) as a light brown oil after column chromatography [SiO_2; EtOAc (10%)/petroleum ether (90%)]: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.32 (t, J = 9 Hz, 1 H), 4.50 (dm, J = 13 Hz, 1 H), 2.58 (t, J = 7 Hz, 2 H), 2.34 (td, J = 7 Hz, 9 Hz, 2 H), 2.00 (m, 6 H), 1.74 (s, 3 H); IR (neat) (cm^{-1}) 2940 (s), 2850 (m), 1698 (sw), 1460 (m), 1435 (m), 1340 (w), 1080 (w); ^{13}C NMR ($CDCl_3$) 208.59, 135.02, 126.03, 35.29, 34.58, 30.08, 29.92, 25.15, 25.05, 23.80 ppm; MS, m/e (relative abundance) 151 (4), 150 (20), 127 (10), 106 (70), 104 (100), 91 (54). Cyclononenone **12** decomposes quickly on standing at room temperature.

β-Scission of *cis*-1,2,3,6,7,7a-Hexahydro-7a-methyl-3a*H*-inden-3a-ol (16). *cis*-1,2,3,6,7,7a-Hexahydro-7a-methyl-3a*H*-inden-3a-ol (**16**) (0.099 g, 0.65 mmol) was treated under general β-scission conditions to yield 6-(3-iodopropyl)-6-methylcyclohex-2-enone (**17**) (0.040 g, 45%) and 6-(3-iodopropyl)-6-methyl-2-hexenoic acid lactone (**18**) (0.035 g, 37%). The products were separated by column chromatography [SiO_2; EtOAc (10%)/petroleum ether (90%), then EtOAc (30%)/petroleum ether (70%)]. 6-(3-Iodopropyl)-6-methylcyclohex-2-enone (**17**) was isolated as a light brown oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.90 (dt, J = 10 Hz, 4 Hz, 1 H), 5.95 (dt, J = 10 Hz, 2 Hz, 1 H), 3.19 (t, J = 8 Hz, 2 H), 2.40 (m, 2 H), 1.5–2.1 (m, 6 H), 1.10 (s, 3 H); IR (neat) (cm^{-1}) 2930 (m), 1675 (s), 1440 (w), 1380 (w), 1220 (w), 1110 (w); ^{13}C NMR ($CDCl_3$) 203.50, 148.46, 128.52, 44.12, 37.56, 33.55, 28.41, 23.15, 21.96, 1.96 ppm; MS, m/e (relative abundance) 278 (44), 151 (44), 151 (44), 109 (56), 107 (33), 83 (44), 81 (100). 6-(3-Iodopropyl)-6-methyl-2-hexenoic acid lactone (**18**) was also isolated as a light brown oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.40 (dt, J = 14 Hz, 4 Hz, 1 H), 6.10 (d, J = 14 Hz, 1 H), 3.24 (t, J = 8 Hz, 2 H), 2.55 (m, 2 H), 1.60–2.30 (m, 6 H), 1.41 (s, 3 H); IR (neat) cm^{-1}) 2930 (s), 1670 (s), 1650 (km), 1400 (m), 1380 (m), 1290 (s), 1190 (s), 1050 (m), 800 (m); ^{13}C NMR ($CDCl_3$) 166.71, 144.50, 123.92, 81.12, 42.55, 35.83, 27.97, (22), 125 (15), 82 (100) ppm.

β-Scission of *trans*-1,2,3,4,7,7a-Hexahydro-3a*H*-inden-3a-ol (22). *trans*-1,2,3,4,7,7a-Hexahydro-3a*H*-inden-3a-ol (**22**) (0.089 g, 0.65 mmol) was treated under general β-scission conditions to yield 6-iodocyclonon-3-enone (**23**) (0.070 g, 41%) and chroman (**24**)[22] (0.013 g, 14%). The products were separated by column chromatography [SiO_2; EtOAc (5%)/petroleum ether (95%)] to give chroman (**24**) as a colorless oil with spectra consistent with those described by Frater and Schmid:[22] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 7.0 (m, 4 H), 4.25 (t, J = 6 Hz, 2 H), 2.85 (t, J = 6 Hz, 2 H), 2.08 (quintet, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 129.80, 127.16, 120.078 116.71, 66.38, 24.88, 22.45 ppm. 6-Iodocyclonon-3-enone (**23**) was isolated as a light brown oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.70 (m, 2 H), 4.32 (m, 1 H), 3.14 (d, d, J = 16 Hz, 6 Hz, 2 H), 2.80 (m, 2 H), 2.48 (m, 2 H), 1.60–2.20 (br m, 4 H); IR (neat) (cm^{-1}) 2950 (m), 1705 (s), 1470 (m), 1440 (m), 1140 (m), 760 (s); ^{13}C NMR ($CDCl_3$) 210.32, 130.00, 124.67, 43.85, 41.24, 36.37, 35.56, 30.41, 22.45 ppm; MS, m/e (relative abundance) 264 (4), 262 (11), 149 (43), 137 (48), 119 (60), 107 (100).

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