obtained from the products 4, would have considerable utility in synthesis.

A mechanism which accounts for the formation of compounds 4 is shown in Scheme I. It features a cyclic transition state (7).[9] In the transition state, coordination of the boron atom of the borane with the oxygen atom of the carbonyl group would lower the energy of activation for nucleophilic attack and concurrently facilitate desilylation. The difference in the reaction course, as a function of the trialkylsilyl group of silyl ketene acetal, may be due to that group's effect on the stability of the transient intermediate 8.[10] The stability of 8 would be enhanced if the trialkylsilyl group were TBDMS rather than TMS. Reduction of the ester group of the transient complex 8 by intramolecular hydride transfer from the borane and retransfer of the TBDMS group would form the acetal complex 9.

Supplementary Material Available: Spectroscopic data for the sulfonamides and compounds 2, 4, 5, and 6 (10 pages). Ordering information is given on any current masthead page.

(9) A similar eight-membered cyclic transition state was proposed by Trost to explain the high selectivity of the Lewis acid mediated aldol reaction. See: Trost, B. M.; Urabe, H. *J. Org. Chem.* **1990**, *55*, 3982.

(10) Additional support for this argument was provided by the experimental finding that mono-TBDM-silylated binaphthol was recovered from the aldol reaction in which a promoter prepared from chiral binaphthol and borane·THF was used. The % ee of the reaction was, however, low.

Control of Ring-Junction Stereochemistry via Radical Cyclization. A New Construction of *trans*-Hydrindans

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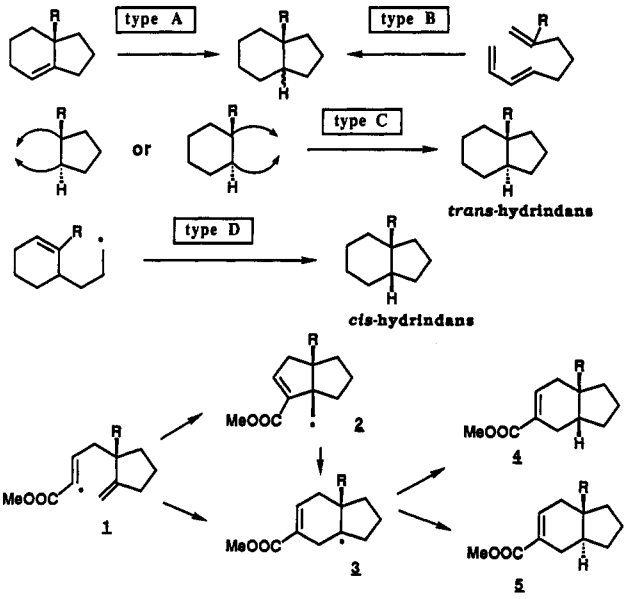
Received January 2, 1991

Summary: Treatment of **7b** with Bu_3SnH in toluene containing Et_3B at −30 °C afforded *trans*-hydrindan **8b** exclusively (97% yield, trans:cis = 100:0). Furthermore, exposure of **13a** to Bu_3SnH in the presence of Et_3B at −30 °C gave the trans angularly methylated hydrindan **14a** in a highly stereocontrolled manner (87% yield, trans:cis = 95:5).

trans-Hydrindans are found in many biologically significant compounds such as steroids and vitamin D derivatives, and therefore, quite a number of synthetic routes to them have been developed. These known synthetic routes may be divided into three types (A,[1] B,[2] and C[3]) as shown in Scheme I.[4] It is noteworthy that in type B control of the ring-junction sterochemistry is achieved at the stage of *trans*-hydrindan ring formation. In the case of angularly methylated hydrindan systems, however, high stereochemical control is rather difficult in general. *exo-trig*-Radical cyclization has been also utilized for the construction of hydrindans (type D), giving *cis*-hydrindans stereoselectively.[5] In this paper, we report a conceptually new synthetic route to *trans*-hydrindans **5** via radical cyclization (Scheme I).

Scheme I



In general, it is known that 1,5-hexadienyl radicals afford kinetically controlled 5-*exo* cyclized products.[5] On the other hand, Beckwith[6] and Stork[7] have reported that these

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(3) (a) Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310. (b) Stork, G.; Winkler, J. D.; Shiner, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 3767. (c) Stork, G.; Saccomano, N. A. *Tetrahedron Lett.* **1987**, *28*, 2087. (d) Takahashi, T.; Shimizu, K.; Doi, T.; Tsuji, J.; Fukazawa, Y. *J. Am. Chem. Soc.* **1988**, *110*, 2674. (e) Takahashi, T.; Shimizu, K.; Doi, T.; Tsuji, J.; Yamamoto, K. *Tetrahedron Lett.* **1989**, *30*, 4999. (f) Doi, T.; Shimizu, K.; Takahashi, T.; Tsuji, J.; Yamamoto, K. *Tetrahedron Lett.* **1990**, *31*, 3313. (g) Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1989**, *111*, 6257. (h) Mikami, K.; Takahashi, K.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 4035. (i) Kim, D.; Kim, S.; Lee, J. J.; Kim, H. S. *Tetrahedron Lett.* **1990**, *31*, 4027. For the synthesis utilizing radical cyclization, see: (j) Dombroski, M. A.; Kates, S. A.; Snider, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 2759. (k) Clive, D. L. J.; Manning, H. W.; Boivin, T. L. B. *J. Chem. Soc., Chem. Commun.* **1990**, 972.

(4) For the synthesis of *trans*-hydrindans using a hydroboration–carbonylation process, see: Brown, H. C.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1968**, 594.

(5) For reviews, see: (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. (b) Neumann, W. P. *Synthesis* **1987**, 665. (c) Curran, D. P. *Synthesis* **1988**, 417, 489. For another type of cis-selective radical cyclization, see: (d) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811. (e) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003. For the *trans*-hydrindan synthesis using radical cyclization of fixed polycyclic ring systems, see: (f) Hart, D. J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.* **1989**, *111*, 7507.

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Table I. Radical Cyclization of 7a, 7b, 13a, and 13b

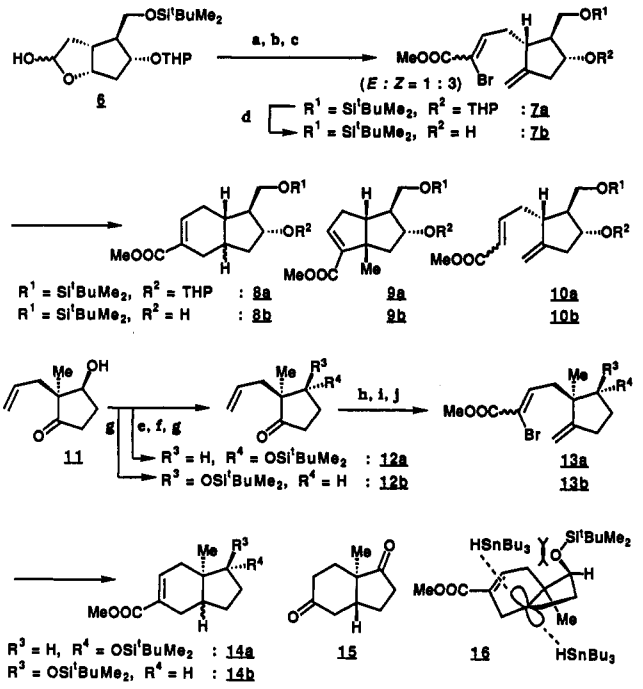
run	substrate	Bu_3SnH (equiv)	radical initiator (equiv)	temp (°C)	time (h)	product:yield (%) 6-endo (trans:cis)	5-exo	reduced
1[a]	**7a**	1.2	Et_3B (0.7)	−50	1.0	**8a**:49 (78:22)	**9a**:33	**10a**:7
2[a]	**7a**	1.2	AIBN (0.07)	120	1.0	**8a**:83 (71:29)		
3[a]	**7b**	1.2	Et_3B (0.2)	−50	3.0	**8b**:23 (100:0)	**9b**:54	**10b**:8
4[a]	**7b**	1.2	AIBN (0.08)	120	0.5	**8b**:72 (63:37)		**10b**:8
5[a]	**7b**	1.7[c]	Et_3B (0.4)	−30	0.5	**8b**:97 (100:0)		
6[a]	**13a**	1.5	Et_3B (0.4)	−30	1.5	**14a**:87 (95:5)	<2	<8
7[b]	**13a**	1.5	Et_3B (0.4)	−70	3.0	**14a**:77 (83:17)	<2	19
8[a]	**13a**	1.5	Et_3B (0.4)	−60	1.5	**14a**:85 (93:7)	<5	<1
9[a]	**13b**	1.2	Et_3B (0.4)	−30	1.5	**14b**:69 (57:43)		5

[a] Reactions were carried out in toluene (4×10^{-3} M). [b] Reactions were carried out in toluene (2×10^{-1} M). [c] Bu_3SnH was added slowly by syringe pump.

radicals provide 6-*endo* cyclized products albeit in modest yields when the hydride concentration is kept low, suggesting the rearrangement of kinetically preferred 5-*exo* cyclized radicals to thermodynamically more stable ones.[8] It was envisioned that cyclization of radicals of type 1[9] under conditions that allow the rearrangement of kinetically controlled products **2** would afford radicals of type **3**, leading to hydrindans. Comparison of the strain energies of **2** and **3**[10] as well as radical stability support this idea. The stereochemistry of the resulting hydrindan would be controlled by the relative stability of two transition states (**3** → **4** and **3** → **5**) in which radicals abstract a hydrogen atom. Supposing that product stability is reflected in the transition state,[11] we predicted that **5** would be produced preferentially.

The stereocontrolled synthesis of the *trans*-hydrindans **8a** and **8b**, which are the key intermediates for biologically interesting *trans*-homoisocarbacyclins,[12] was investigated first. Toward this end, bromo esters **7a** and **7b**[13] were efficiently synthesized from the Corey lactone as shown in Scheme II. Treatment of **7a** (*E*:*Z* = 1:3) with Bu_3SnH in toluene (4×10^{-3} M) at 120 °C (run 2, Table I) afforded only *endo*-cyclized products (**8a**, 83%) in a ratio of 71:29 (trans–cis)[14] without producing the *exo*-cyclized isomer **9a**. Lowering the reaction temperature to −50 °C, however, resulted in the formation of **9a** (33%) accompanied by **8a** with slightly improved stereoselectivity (trans:cis = 78:22). On the other hand, exposure of **7b** (*E*:*Z* = 1:3) to Bu_3SnH at −50 °C (run 3, Table I) furnished **8b** in a highly stereoselective manner (trans (R_f value 0.32, silica gel plate, ether–hexane (2:1)):cis (R_f value 0.38) = 100:0) albeit in low yield. The low yield of **8b** was greatly improved by slow continuous addition of the hydride reagent. That is, Bu_3SnH (1.2 equiv) in toluene (5 mL) was slowly added by a syringe pump over 0.5 h to a stirred solution of **7b**

Scheme II[a]



[a] Ph_3P=CBrCOOMe (1.8 equiv), toluene, 80 °C, 18 h (97%).[23] [b] $(COCl)_2$ (3 equiv), DMSO (6 equiv), NEt_3 (10 equiv) (95%). [c] $ZnCH_2Br_2TiCl_4$, CH_2Cl_2, rt, 1 h (78%).[24] [d] Et_2AlCl (5 equiv), CH_2Cl_2, 0 °C, 30 min (85%). [e] DEAD (2.7 equiv), PPh_3 (2.1 equiv), 3,5-dinitrobenzoic acid (2.0 equiv), THF, rt, 16 h (99%).[25] [f] K_2CO_3 (0.3 equiv), MeOH, rt, 12 h (100%). [g] *t*-$BuMe_2SiCl$ (1.8 equiv), imidazole (1.8 equiv), DMF, rt, 12 h (**12a**, 100%; **12b**, 99%). [h] O_3, MeOH, −78 °C, 1.5 h then Me_2S (3.7 equiv), rt, 4 h. [i] Ph_3P=CBrCOOMe (2.3 equiv), THF, 70 °C, 4.5 h (2 steps, from **12a**, 91%; **12b**, 67%). [j] $ZnCH_2Br_2TiCl_4$, CH_2Cl_2, rt, 1.5 h (**13a**, 61%; **13b**, 63%).

(0.56 mmol) and Et_3B[15] (0.4 equiv) in toluene (4×10^{-3} M) at −30 °C, giving **8b** (97%) in a highly stereoselective manner (trans:cis = 100:0).[16] The structure and stereochemistry of *trans*-**8b** and *cis*-**8b** were determined by spectral data including ^1H NMR, ^{13}C NMR, IR, MS, and HRMS (see supplementary material). The ring-junction carbons of *cis*-**8b** (δ 27.18, 27.78) are more shielded than those of *trans*-**8b** (δ 30.91, 31.05), which is in accord with the fact that the ^{13}C NMR shift values for a trans ring junction are greater than those for a cis junction.[17] Furthermore, the stereochemistry of *cis*-**8b** was confirmed

(7) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529.
(8) For other *endo*-selective radical cyclizations, see: (a) Broka, C. A.; Reichert, E. C. *Tetrahedron Lett.* **1987**, *28*, 1503. (b) Takano, S.; Suzuki, M.; Kijima, A.; Ogasawara, K. *Chem. Lett.* **1990**, 315.
(9) α,β-Unsaturated ester group was expected to be converted to various functional groups.
(10) Strain energies of the stable conformers were calculated by MM2(85): **2** (R = H), 22.5 kcal/mol; **3** (R = H), 19.7 kcal/mol. The torsional and bending parameters for the carbon radical were approximated by those of an sp^2 carbon.
(11) Strain energies of the stable conformers were calculated by MM2(85): **4** (R = H), 21.0 kcal/mol; **5** (R = H), 18.7 kcal/mol.
(12) Takahashi, A.; Shibasaki, M. *Tetrahedron Lett.* **1987**, *28*, 1893. (b) Shibasaki, M.; Takahashi, A.; Aoki, T.; Sato, H.; Narita, S. *Chem. Pharm. Bull.* **1989**, *37*, 1647.
(13) Calculations by MM2(85) showed that *trans*-**8a**′ (R^1 = $SiMe_3$, R^2 = THP) and **8b**′ (R^1 = $SiMe_3$, R^2 = H) are 0.9 and 2.6 kcal/mol more stable than the cis isomers, respectively.
(14) A mixture of the products was treated with Et_2AlCl[22] in CH_2Cl_2 (0 °C, 50 min) to give *trans*-**8b** and *cis*-**8b** (93% yield), which were separable by silica gel column chromatography.
(15) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547.
(16) **8a** and **8b** were converted to various homoisocarbacyclins. The biological activities will be reported in due course.
(17) Metzger, P.; Casadevall, E.; Pouet, M. J. *Org. Magn. Reson.* **1982**, *19*, 229.

by conversion to homoisocarbacyclin.[12] It should be mentioned that these results are in full accord with MM2 calculations[13] (Scheme II, Table I).

Encouraged by this excellent result, we then turned our attention to the stereocontrolled construction of trans angularly methylated hydrindans, which are known to be very important as steroidal intermediates. Bromo esters **13a** and **13b** were efficiently prepared as shown in Scheme II.[18] MM2 calculations show that *trans*-hydrindans **14a** and **14b** would be produced under the thermodynamically controlled conditions (*trans*-**14a**′ (R^3 = H, R^4 = $OSiMe_3$) and **14b**′ (R^3 = $OSiMe_3$, R^4 = H) are 1.3 and 0.7 kcal/mol more stable than the cis isomers, respectively). As expected, treatment of **13a** (*E*:*Z* = 1:7) with Bu_3SnH in toluene (4.0×10^{-3} M) at −30 °C for 1.5 h produced the desired *trans*-hydrindan **14a** stereoselectively (87%, trans:cis = 95:5),[19] a potential intermediate for various steroids such as adrenosterone, together with the reduced product (<8%) and the 5-*exo* cyclized product (<2%) (run 6, Table I). The previous reaction when carried out at −70 °C and at much higher concentration (2.0×10^{-1} M) gave the same three cyclization products (6-endo-trans, 6-endo-cis, and 5-exo) in a similar ratio (run 7, Table I).[20] This result appears to indicate that the alkenyl radical produces the hydrindan radical directly owing to steric factors. The stereochemistry of *trans*-**14a** and *cis*-**14a** was unequivocally determined by conversion to the known diketone **15** in six steps (i. Pd/C, H_2, ii. LDA, O_2, iii. $LiAlH_4$, iv. $NaIO_4$, v. TBAF, vi. PCC-MS4A, 26% overall yield).[1a] On the other hand, exposure of **13b** (*E*:*Z* = 1:4) to Bu_3SnH at −30 °C (run 9, Table I) gave hydrindans **14b** with much lower stereoselectivity (trans:cis = 57:43), indicating that there is severe steric repulsion between the (*tert*-butyldimethylsilyl)oxy group and Bu_3SnH in the transition state **16**.[21]

In conclusion, a conceptually new synthetic route to *trans*-hydrindans has been developed by a novel type of radical cyclization. The present methodology should be useful for construction of other ring systems. In addition, it has been successfully demonstrated that MM2 calculations are useful for the design of radical cyclization substrates.

Supplementary Material Available: Experimental procedures for the preparation of compounds **7b**, **8b**, **12a**, **13a**, and **14a** (7 pages). Ordering information is given on any current masthead page.

(18) Brooks, D. W.; Grothaus, P. G.; Irwin, M. L. *J. Org. Chem.* **1982**, *47*, 2820. For convenience, 11 with the opposite configuration from that of steroids was used.
(19) Use of the syringe pump technique did not improve the result.
(20) In general, slightly lower stereoselectivity was obtained at lower reaction temperature. The reason is not clear at present.
(21) Although the reason is not clear at present, treatment of **13b** with Bu_3SnH at −60 °C produced **14b** in a trans–cis (30:70) ratio.
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(23) Gonzalez, M. S. P.; Aciego, R. M. D.; Herrera, F. J. L. *Tetrahedron* **1988**, *44*, 3715.
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The Photochemistry of Diphenyliodonium Halides: Evidence for Reactions from Solvent-Separated and Tight Ion Pairs

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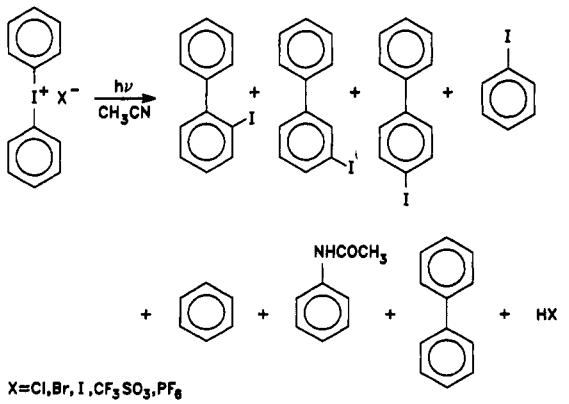
Received January 11, 1991

Summary: Diphenyliodonium halides exist as tight ion pairs in acetonitrile, and photolysis gives almost exclusively iodobenzene by a homolytic cleavage reaction from a charge transfer excited state, whereas in aqueous acetonitrile the ion pairs are solvent separated and photolysis gives substantial amounts of 2-, 3-, and 4-iodobiphenyls, in addition to iodobenzene, by an initial heterolytic cleavage.

Onium salts have found important applications as photoinitiators for acid-catalyzed processes in polymers.[1] Recent mechanistic studies have found that onium salt photolysis produces acid by both in-cage recombination reactions and cage-escape reactions with solvent.[2-7] We have recently reported that direct photolysis of diaryliodonium salts produces 2-, 3-, and 4-iodobiphenyls, io-

Scheme I. Products from Photolysis of Diphenyliodonium Salts in Acetonitrile and Aqueous Acetonitrile



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