Oxyfunctionalization of Non-Natural Targets by Dioxiranes. 2. Selective Bridgehead Dihydroxylation of Fenestrindane[1]

Caterina Fusco, Michele Fiorentino, Anna Dinoi, and Ruggero Curci*

Centro CNR "MISO", Dipartimento Chimica, Università di Bari, Via Amendola 173, I-70126 Bari, Italy

Ralph A. Krause and Dietmar Kuck*,†

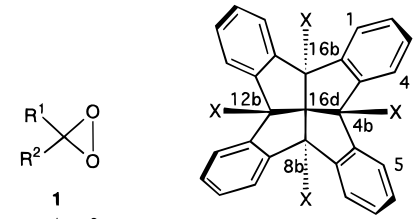
Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, D-33615 Bielefeld, Germany, and Universität-Gesamthochschule Paderborn, Warburger Strasse 100, D-33098 Paderborn, Germany

Received July 12, 1996[⊗]

Introduction

The regioselective functionalization of complex molecular framework is an important goal in organic synthesis; in particular, the bridgehead functionalization of polycyclic compounds can provide access to derivatives bearing quaternary carbon centers or strained bridgehead double bonds. In this context, the controlled functionalization of centropolyindanes[1−3] at their benzylic and/or benzhydrylic bridgehead positions is of particular interest since it allows the synthesis of complex three-dimensionally fused polyquinane carbon skeletons, including highly strained cycloolefins such as those of the acepentalene family.[4,5]

Dioxiranes (**1**)[6] have been proven to be useful reagents for the selective oxidation of a variety of polycyclic hydrocarbons under mild conditions.[6−9] In addition to representative alicyclic systems (e.g., the decalins,[7,8a] adamantane,[8b] and 2,4-didehydroadamantane[9]) they have been applied to the selective oxyfunctionalization of natural target compounds, such as vitamin D_3 derivatives[10a] and several steroids.[10b,c] To carry out these oxidations, methyl(trifluoromethyl)dioxirane (**1b**)[11] is often the reagent of choice, since it provides higher substrate conversions and shorter reaction times with respect to dimethyldioxirane (**1a**)[12] with no loss in selectivity.[6a]



We have shown recently that representative centropolyindanes undergo selective oxygen atom insertion into their bridgehead C−H bonds by dioxiranes.[1] In particular, by varying the excess of the methyl(trifluoromethyl)dioxirane (**1b**) reagent, tetrabenzo[5.5.5.5]-fenestrane (fenestrindane) (**2**)[13] could be converted either into the corresponding monoalcohol or into the corresponding all-bridgehead tetraalcohol, i.e., 4b,8b,12b,16b-tetrahydroxyfenestrindane (**3**);[1,14] the oxidation products were isolated and characterized as the corresponding mono- and tetraacetate, respectively.[1]

As an expansion on this breakthrough, it appeared convenient to explore the access to fenestrindanes being only partially functionalized at the bridgeheads, since these are foreseen to be valuable intermediates on the way to the highly unsaturated fenestrindanes containing strained isoindene moieties.[15−17] In this context, the elucidation of the stereo- and regiocontrol in the sequence of multiple oxyfunctionalization of fenestrindane appeared of varied interest. We report herein on the selective 2-fold bridgehead oxyfunctionalization of fenestrindane **2** using the powerful dioxirane **1b**, along with kinetic data that provide useful hints concerning the mechanism of the oxygen insertion reaction.

Results and Discussion

Fenestrindane Dihydroxylation Using Methyl(trifluoromethyl)dioxirane. Treatment of **2** with a ca.

† University of Paderborn.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

(1) Part 1: Kuck, D.; Schuster, A.; Fusco, C.; Fiorentino, M.; Curci, R. *J. Am. Chem. Soc.* **1994**, *116*, 2375.

(2) Schuster, A.; Kuck, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1699.

(3) For accounts on centropolyindane chemistry, see: (a) Kuck, D. *Synlett* **1996**, in press. (b) Kuck, D. In *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*; Hargittai, I., Ed.; VCH: New York, 1990; Chapter 19.

(4) (a) Kuck, D.; Schuster, A.; Paisdor, B.; Gestmann, D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 721. (b) Kuck, D.; Schuster, A.; Gestmann, D.; Posteher, F.; Pritzkow, H. *Chem. Eur. J.* **1996**, *2*, 58. (c) Kuck, D.; Schuster, A.; Gestmann, D. *J. Chem. Soc., Chem. Commun.* **1994**, 609.

(5) (a) Haag, R.; Ohlhorst, B.; Noltemeyer, M.; Fleischer, R.; Stahlke, D.; Schuster, A.; Kuck, D.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 10474. (b) Kuck, D.; Schuster, A.; Ohlhorst, B.; Sinnwell, V.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 595. (c) Haag, R.; Ohlhorst, B.; Noltemeyer, M.; Schuster, A.; Kuck, D.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1727. (d) Haag, R.; Kuck, D.; Fu, X.-Y.; Cook, J. M.; de Meijere, A. *Synlett* **1994**, 340.

(6) For recent reviews on dioxirane reactivity, see: (a) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67* , 811. See references to the pertinent articles quoted therein. (b) Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; Chapter 4, pp 195−219. See references therein.

(7) Murray, R. W.; Jeyaraman, R.; Mohan L. *J. Am. Chem. Soc.* **1986**, *108*, 2470.

(8) (a) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749. (b) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 3067−3070.

(9) Teager, D. S.; Murray, R. K., Jr. *J. Org. Chem.* **1993**, *58*, 5548.

(10) (a) Curci, R.; Detomaso, A.; Prencipe, T.; Carpenter, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 8112. (b) Bovicelli, P.; Lupattelli, P.; Mincione, E.; Prencipe, T.; Curci, R. *J. Org. Chem.* **1992**, *57*, 2182. (c) Bovicelli, P.; Lupattelli, P.; Mincione, E.; Prencipe, T.; Curci, R. *J. Org. Chem.* **1992**, *57*, 5052.

(11) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890.

(12) (a) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. (b) Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1987**, *52*, 699.

(13) (a) Kuck, D. *Chem. Ber.* **1994**, *127*, 409. (b) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* **1986**, *108*, 8107.

(14) Kuck, D.; Schuster, A.; Krause, R. A. *J. Org. Chem.* **1991**, *56*, 3472.

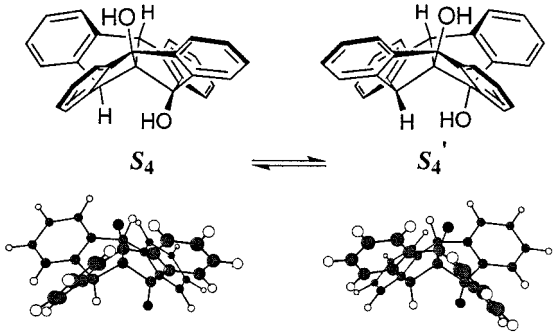
(15) [5.5.5.5]Fenestranes containing more than four double bonds in the fenestrane core have been discussed in the literature (ref 16) in the context of the planar-tetracoordinate-carbon problem (ref 17).

(16) (a) Gupta, A. K.; Fu, X.; Snyder, J. P.; Cook, J. M. *Tetrahedron* **1991**, *47*, 3665. (b) Luef, W.; Keese, R. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: Greenwich, CT, 1993; Vol. 3, pp 229−267. (c) Chadrasekhar, J.; Würthwein, E. U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921. (d) Würthwein, E.-U.; Chadrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 843. (e) Böhm, M. C.; Gleiter, R.; Schang, P. *Tetrahedron Lett.* **1979**, *20*, 2575.

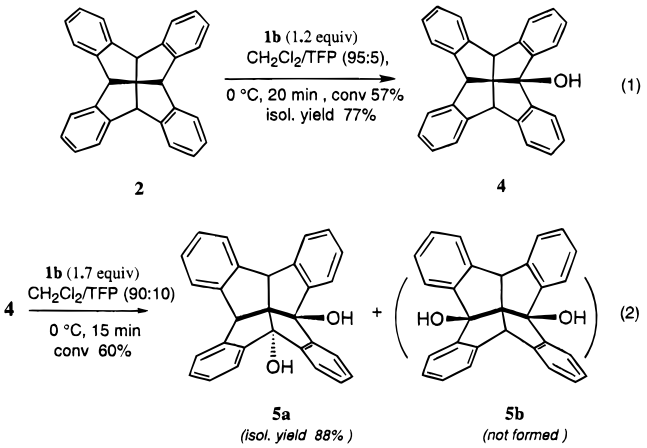
(17) (a) Hoffmann, R.; Alder, R.; Wilcox, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (b) Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181.

S0022-3263(96)01316-3 CCC: $12.00

Scheme 1. Conformational Equilibrium between the Two Rotamers of Fenestranediol 5a (S_4 Symmetry Notation Refers to the Carbon Skeleton Only)



0.82 M solution of methyl(trifluoromethyl)dioxirane (**1b**) (1.5 equiv) at the conditions given in eq 1 resulted in a ca. 60% substrate conversion within 20 min, yielding the monoalcohol **4**[1] as the only product (isolated yield 77%, based on converted **2**).



Then, isolated **4** was allowed to react with an additional 1.7 equiv of **1b** under similar conditions (eq 2). Within 15 min, a 60% conversion of the starting material was attained (GC/MS monitoring); from the reaction mixture a dialcohol could be isolated in 88% yield (based on converted **3**). This novel derivative was identified as 4b,8b-dihydroxyfenestrindane **5a**, i.e., the regioisomer bearing both hydroxyl groups at one and the same indane unit. Its regioisomer **5b** bearing the hydroxy groups at the 4b,12b-bridgehead positions was not detected in the reaction mixture.

The identity of diol **5a** could be unambigously established on the basis of its ^{1}H and ^{13}C NMR spectra, as well as by EI and FAB mass spectrometry. In fact, while the FAB mass spectrum (NBA/NaI) does show the (quasi) molecular ion ($[M + Na]^+$, *m*/*z* 423), the EI mass spectrum exhibits no significant molecular ion peak ($M^{\bullet+}$, *m*/*z* 400), but it displays an intense $[M - H_2O]^{\bullet+}$ signal (*m*/*z* 382) as the base peak. As recorded for a number of similar cases in centropolyindane chemistry[18] and indeed recorded for the precursor alcohol **4** itself, an extremely fast water loss from $M^{\bullet+}$ ions[19] points to a stereochemical disposition having a weakly bound hydrogen atom in a favorable 1,3-*syn* orientation with respect to a hydroxyl group; this feature is presented twice (once each face) by the 4b,8b-diol **5a**. Thus, it is unlikely that the isolated diol has instead the structure of the 4b,12b-diol **5b**, since the said stereospecific water elimination processes would not be expected for its gaseous molecular radical cation.[20]

The NMR spectra of the diol **5a** corroborate the structure assignment; in fact, they also allow one to rule out the alternative structure **5b**, provided one makes the assumption that the two possible conformers of the [5.5.5.5]fenestrane skeleton undergo fast equilibration on the NMR time scale (Scheme 1). This assumption should hold safely for both diols **5a** and **5b**; in fact, even tetraol **3**—which bears *two* sets of 1,3-*syn* diol groupings—has been shown to be conformationally relatively flexible.[14,21]

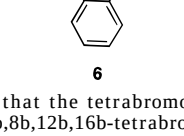
Given this conformational flexibility, the apparent molecular symmetry of 4b,8b-diol **5a** and of 4b,12b-diol **5b** would be C_2 and C_{2v}, respectively. Then, both the ^{1}H and the ^{13}C NMR spectra of the dialcohol product indicate that it has the 4b,8b-diol structure **5a**, while they rule out the corresponding regioisomer **5b**. Indeed, the ^{13}C NMR spectrum displays just three (of the four possible) resonance lines for the carbon atoms of the intraindan bonds and all of the eight lines expected for the remaining benzo nuclei resonances in **5a**. By way of contrast, 4b,12b-diol **5b** would exhibit only a set of two and four resonances for the quaternary and tertiary carbon atoms of the benzo nuclei, respectively. Careful inspection of the ^{1}H NMR and the COSY-^{1}H−^{1}H spectra of the diol isolated reveals the presence of two distinct AA′BB′ spin systems along with two identical ABCD spin systems; this also points to apparent C_2 molecular symmetry, as indeed presented by **5a**. Thus, the further dioxirane hydroxylation of monoalcohol **4** occurs with surprising high regio and facial selectivity at the back side of the [5.5.5.5]fenestrane core to yield exclusively the 4b,8b-diol **5a**.

Kinetics and Mechanism. Rate data were gathered in order to gain insight into the nature of the *O*-insertion reactions at hand. In the kinetic experiments performed with comparable initial concentrations of substrate and oxidant under "normal" conditions (i.e., air blanket, protection from light), the rate of dioxirane consumption with time was monitored (iodometry); the formation of products was verified by GC and/or GC/MS. In all of the cases examined, the kinetics were found to obey a clean overall second-order rate-law (order one each in dioxirane and fenestrindane **2** or **4**); integrated second-order rate law plots were found to be linear to over 80% reaction, yielding reproducible k_2 values. In Table 1 rate data are collected for the transformation of fenestrindane **2** into its monoalcohol **4** and in turn of this into diol **5a**, along

(18) Kuck, D.; Neumann, E.; Schuster, A. *Chem. Ber.* **1994**, *127*, 151.

(19) For a general discussion of stereospecific water elimination processes in gaseous radical cations of alcohols, see: Mandelbaum, A. In *Stereochemistry*; Kagan, H. B., Ed.; Thieme: Stuttgart, Germany, 1977; Vol. 1, pp 153 ff.

(20) Direct support for this assumption is given by the recent finding that 8b,16b-centropentaindane diol (**6**), a derivative of **5b** bearing two strictly 1,3-*syn* oriented hydroxy groups, exhibits only moderate water loss upon EI-MS, i.e., ($[M]^{\bullet+}/[M - H_2O]^{\bullet+}$) ca. 0.5 (ref 4b).



6

(21) It is interesting that the tetrabromo analog of tetrahydroxyfenestrindane (**3**), i.e., 4b,8b,12b,16b-tetrabromofenestrindane, instead behaves as in an apparently *static* equilibrium of two conformers with S_4 molecular symmetry on the NMR time scale. Clearly, the presence of bulky bromine atoms at the bridgehead positions effectively restrains conformational equilibration of the [5.5.5.5]fenestrane skeleton. (See, e.g.: Kuck, D.; Schuster, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1192.)

Table 1. Kinetic Data and Relative Rates for *O*-Insertion by Dioxirane 1b into Benzhydrylic C−H Bonds of Selected Substrates in Acetone at 0.0 ± 0.1 °C

entry	substrate	$10^2 k_2$[a] (M^{-1} s^{-1})	rel rate per H[b]
1	fenestrindane (**2**)	9.37 ± 0.03	0.57[c]
2	4b-fenestrindanol (**4**)	13.9 ± 0.04	1.7[d]
3	$PhCH(CH_3)2$ (**7**)	4.10 ± 0.02	1.0
4	$Ph_2CH(CH_3)$ (**8**)	2.50 ± 0.05	0.61

[a] Kinetic constants calculated from integrated second order rate-law plots that were linear to over 80% reaction; average values shown are from two or more independent runs agreeing within ±5%. [b] From kinetic constants divided by the appropriate statistical factor. [c] Statistical factor of 4 (four equivalent benzhydrylic C−H). [d] A statistical factor of two applies here since only insertion into the two benzhydrylic C−H *anti* to the OH group of **4** can lead to the anti diol **5a** (the sole reaction product).

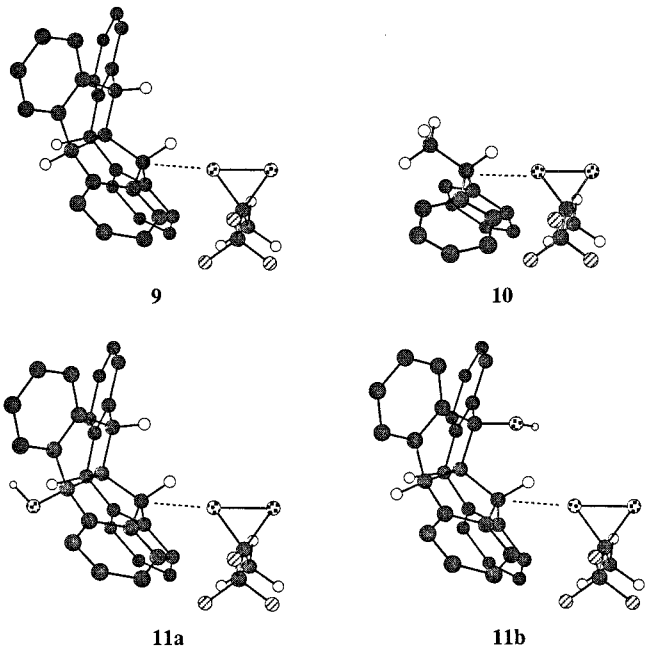
with the oxidation rates measured for cumene (**7**) and 1,1-diphenylethane (**8**).

Similar to fenestrindane (**2**), the oxyfunctionalization of these reference compounds **7** and **8** occurs selectively at the benzhydrylic C−H bonds.[7,8b,22] In none of the cases examined could the presence of esters ROAc[23] or ROC(:O)CF_3, nor (in the case of substrates **7**) of acetophenone $PhC(:O)CH_3$, be revealed (GC and ^1H NMR) in the reaction mixture. Should the reaction involve free radicals, formation of these side products is to be expected.[23] Furthermore, the oxidation of 1,1-diphenylethane (**8**) is *slower* than that of cumene (**7**) (Table 1, entries 3 and 4); this is also at odds with the expectation[23] of free-radical involvement in view of the higher stability of $Ph_2(CH_3)C^\bullet$ with respect of $Ph(CH_3)_2C^\bullet$.[24]

These facts and the simple kinetics observed rule out the recent claim by Minisci et al.[23] that under the conditions adopted the *O*-insertion into C−H bonds proceeds via a *free*-radical chain mechanism. Instead, findings herein—alongside with previous[8a,25] and recent evidence,[26] including the application a radical-clock probe by the Ingold group[27] —provide further support to our earlier proposal[8] of a rather concerted *O*-insertion into C−H bonds *in the rate-determining step*, possibly leading to radical pairs capable of *fast* in-cage collapse ("oxygen rebound").[6a] In line with this, we have reported[25] that the transformation of optically active (*S*)-(−)-2-phenylbutane Ph(Et)(Me)C*H into the corresponding alcohol Ph(Et)(Me)C*OH by dioxirane **1b** occurs in high yield with complete retention of configuration and no loss of optical purity.

Once a free-radical chain mechanism is discounted, a rationalization of the kinetic and stereochemical data can be attempted on the grounds of a previously described transition-state (ts) model for the rate-determining *O*-insertion.[1] On the basis of careful ab initio calculations and FMO analysis,[28] this envisages electrophilic attack by the dioxirane to be directed along the O−O bond axis at the carbon atom of the C−H bond; the latter should be favorably oriented to shift the H atom to the approaching oxygen, which employs an electron pair as

Chart 1



migration terminus while the O−O bond is being broken.[28] According to this preferential direction of approach, as shown by ts structures **9** and **10** (Chart 1), fenestrindane (**2**)—despite its complex architecture—should present no additional steric hindrance to stereoalignment with respect to 1,1-diphenylethane (**8**). Indeed, after the statistical factor is taken into account, the hydroxylation rate for the two substrates is practically identical (Table 1, entries 1 and 4).

Of particular interest is the case of fenestrindanol (**4**) hydroxylation, leading selectively to the corresponding 4b,8b-diol **5a** only. In fact, stereoselectivities in dioxirane epoxidations of allylic and homoallylic alcohols have been rationalized in terms of opposing steric effects and cooperative H-bonding exercised by the OH functionality in the ts, sometimes with conflicting outcome.[6a] For instance, Murray, Singh, et al. have reported a rather clear-cut case of OH participation in the dioxirane epoxidation of homoallylic $-CH_2OH$-substituted cyclohexene, leading to distinct *syn*-facial selectivity.[29] More recently, Adam and Smerz have discussed the regio- and diastereoselective epoxidations of acyclic allylic alcohols by dimethyldioxirane (**1a**) in terms of intramolecular H-bonding with the incoming dioxirane.[30] On the other hand, dioxirane epoxidations of allylic alcohols possessing sufficient conformational rigidity and of 4β-hydroxycholesterol[31] (as well as other steroids[32]) were found to proceed largely with *anti* stereochemistry. Since dioxiranes are highly polar species (cf., μ = 2.5 D for the parent dioxirane H_2CO_2),[6] it is also recognized that specific solvation and electrostatic effects (such as dipole−dipole interactions) in the ts could become a major factor in determining stereoselectivity of dioxirane epoxidations.[6a]

In addition to the OH functionality, fenestrindanol **4** contains only benzhydrylic C−H bonds at the bridgehead positions, each pointing to one or the other of the two concave molecular surfaces in this centropolyindane. If

(22) Kuck, D.; Schuster, A. *Z. Naturforsch.* **1991**, *46B*, 1223.
(23) (a) Bravo, A.; Fontana, F.; Fronza, G.; Mele, A.; Minisci, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1573. (b) Minisci, F.; Zhao, L.; Fontana, F.; Bravo, A. *Tetrahedron Lett.* **1995**, *36*, 1697.
(24) See, e.g.: Robaugh, D. A.; Stein, E. S. *J. Am. Chem. Soc.* **1986**, *108*, 3224 and references therein.
(25) Adam, W.; Asensio, G.; Curci, R.; Gonzalès-Nuñez, M. E.; Mello, R. *J. Org. Chem.* **1992**, *57*, 953.
(26) Curci, R.; Dinoi, A.; Fusco, C.; Lillo, M. A. *Tetrahedron Lett.* **1996**, *37*, 249.
(27) Vanni, R.; Garden, S. J.; Banks, J. T.; Ingold, K. U. *Tetrahedron Lett.* **1995**, *36*, 7999.
(28) Bach, R. D.; Andrés, J. L.; Owensby, A. L.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5768.
(29) Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *J. Org. Chem.* **1996**, *61*, 1830.
(30) Adam, W.; Smerz, A. K. *J. Org. Chem.* **1996**, *61*, 3506.
(31) Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. *J. Org. Chem.* **1982**, *47*, 2670.
(32) Marples, B. A.; Muxworthy, J. P.; Baggaley, K. H. *Tetrahedron Lett.* **1991**, *32*, 533.

the hydroxyl group were to excercise cooperative H-bonding to the approaching dioxirane, face-selective oxyfunctionalization at the C-H in 1,3-*syn* orientation with respect the OH group is expected. By way of contrast, the opposite stereochemical course is verified since the *anti* diol **5a** is produced exclusively. Inspection of the likely ts arrangements (Chart 1) provides a clue. In fact, for *syn* hydroxylation to occur with the given stereoalignment, the hydroxy group is in no position to assist the approaching dioxirane by cooperative H-bonding (cf.,**11b**). Then, the hydroxylation preferentially occurs with *anti* stereochemistry (**11a**), perhaps with such an orientation of the existing OH moiety that *O*-insertion from the opposite face becomes favored by electrostatic interactions. This would explain the noticeable increase in rate on going from **2** to **4** (Table 1).

Conclusions

Our results support the notion that—provided one avoids conditions that trigger free-radical decomposition of the peroxide[23,26]—dioxirane oxyfunctionalizations can lead to remarkable regio- and *anti*-facial selectivity.[6a] Data presented herein corroborate the view that, along with steric effects, electrostatic effects (such as dipole−dipole interactions) in the ts might become a relevant factor in discriminating between *anti* and *syn* attack of functionalized substates by the dioxirane, favoring an *anti* stereochemistry in the case of 4b-hydroxyfenestrindane at hand.

Apart from the mechanistic clues, the feat of partial oxyfunctionalization of fenestrindane **2** at two bridgehead positions belonging to the same indan unit by using methyl(trifluoromethyl)dioxirane paves the road to explore the conversion into other 4b,8b-disubstituted fenestrindanes, hence into the corresponding isoindenes,[33] and novel [5.5.5.5]fenestranes bearing two unsaturated bridgehead positions.[2,5,15] The attainment of these targets remains a challenging goal in the chemistry of centropolyindanes.

Experimental Section

Methylene chloride, acetone, and 1,1,1-trifluoro-2-propanone (TFP) (bp 22 °C) were purified by standard methods,[1] stored over 5 Å molecular sieves at 2−5 °C, and routinely redistilled prior to use. Curox triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (a gift by Peroxid-Chemie GmbH, Munich, Germany) was our source of potassium peroxymonosulfate to be employed in the synthesis of dioxiranes. Solutions of 0.8−1.0 M methyl(trifluoromethyl)-dioxirane (**1b**)[8,11] in TFP were obtained by adopting procedures, equipment, and precautions already described in detail. High purity commercial (Aldrich) cumene and 1,1-diphenylethane were further purified by distillation. The synthesis and spectral characteristics of 4bα,8b*β*,12bα,16b*β*-tetrahydrodibenzo[*a*,*f*]-dibenzo[2,3;4,5]pentaleno[1,6-*cd*]pentalene (fenestrindane) (**2**) have been given.[13] Melting points were not corrected. Equipment and analytical methods have been previously reported.[1]

Stepwise Dihydroxylation of Fenestrindane (2) Using Methyl(trifluoromethyl)dioxirane (1b). To a stirred solution of **2** (150 mg, 0.407 mmol) in CH_2Cl_2 (15 mL) kept at 0 °C was gradually added a standardized solution of 0.82 M dioxirane **1b** (0.6 mL, 0.490 mmol) in TFP. As monitored by GC or GC/MS [column SE 30, 30 m × 0.25 mm i.d., temperature program 240 °C (5 min), 240−280 °C (10 °C/min)], during 20 min over 50% substrate conversion was achieved. Removal of the solvent in vacuo followed by column chromatography (silica gel, $CHCl_3$) afforded recovery of the starting material (65 mg, 0.176 mmol) and the monoalcohol **4** (68 mg, 0.177 mmol, 77% yield based on converted **2**).

4b-Hydroxy-4bα,8b*β*,12bα,16b*β*-tetrahydrodibenzo[*a*,*f*]-dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (4): colorless solid; mp 258−260 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (m, 2 H, 4/5-*H*), 7.53 (m, 4 H), 7.49 (m, 2 H), 7.34 (m, 4 H), 7.25 (m, 4 H), 5.23 (s, 1 H, 12b-*H*), 4.71 (s, 2 H, 8b/16b-*H*), 2.20 (s, 1 H, O*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 145.24 (s), 144.72 (s), 144.00 (s), 143.84 (s), 129.28 (d), 128.17 (d), 127.73 (d), 127.45 (d), 124.67 (d), 124.56 (d), 124.48 (d), 124.28 (d), 92.31 (s, *C*-4b), 75.34 (*C*-16d), 60.93 (d, *C*-8b/16b), 54.65 (d, *C*-12b); MS (EI, 70 eV) *m*/*z* (r.i.) 366 (100, $[M - H_2O]^{\bullet+}$), 364 (12), 363 (21), 350 (9), 289 (7), 183 (10, $[M - H_2O]^{2+}$), 181 (11), 180 (7), 175 (15), 168 (7). Anal. Calcd. for $C_{29}H_{20}O$: C, 90.6; H, 5.24. Found: C, 89.5; H, 5.31.

Next, a cool aliquot of 0.50 M dioxirane **1b** in TFP (0.8 mL, 0.400 mmol) was added to a stirred solution of the above-described monoalcohol **4** (90 mg, 0.230 mmol) in CH_2Cl_2 (7 mL) at 0 °C; GC/MS monitoring of the reaction mixture indicated 60% starting material conversion after 15 min and formation of diol **5a** as essentially the sole product. Removal of solvent and column chromatography (silica gel, $CHCl_3$) allowed recovery of the monoalcohol **4** (38 mg, 0.100 mmol) and isolation of diol **5a** (46 mg, 87% yield based on converted **4**).

4b,8b-Dihydroxy-4bα,8b*β*,12bα,16b*β*-tetrahydrodibenzo-[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (5a): colorless solid; mp 275−278 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), ^{1}H−^{1}H COSY (300 MHz): δ 7.72 (m, 2 H, 5/8-*H*), 7.68 (m, 2 H, 4/9-*H*), 7.54 (m, 2 H, 1/12-*H*), 7.50 (m, 2 H, 13/16-*H*), 7.41 (m, 2 H, 6/7-*H*), 7.33 (m_c, 4 H, 3/10/2/11-*H*), 7.24 (m, 2 H, 14/15-*H*), 5.21 (s, 2 H, 12b/16b-*H*); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 145.3 (s), 144.91 (s), 144.51 (s, 2 C), 129.91 (d), 129.55 (d), 128.05 (d), 127.63 (d), 124.76 (d), 124.43 (d), 124.38 (d), 124.15 (d), 91.31 (s, *C*-4b/8b), 78.56 (*C*-16d), 53.75 (d, *C*-12b/16b); MS (EI, 70 eV) *m*/*z* (r.i.) 382 (100, $[M - H_2O]^{\bullet+}$), 366 (10), 365 (10), 354 (19), 352 (16), 351 (10), 350 (11), 276 (9), 190.5 (15, $[M - H_2O]^{2+}$), 181 (10); HRMS (FAB^+, 3-nitrobenzyl alcohol/NaI) 423.1365 of $[M + Na]^+$, calcd for $C_{29}H_{20}O_2$ + Na 423.1361.

Kinetic Measurements. Runs were performed by following the decay of dioxirane concentration (by iodometry) with time, according to described analytical techniques.[8,11] Absolute rates were determined under second-order conditions, with the dioxirane and hydrocarbon initial concentrations kept in the range (4−6) × 10^{-2} M, and differing by 8−20%. At zero time an aliquot (0.5−1.0 mL) of a thermostated dioxirane **1b** solution was added to 10−20 mL of a solution (also thermostated) of the given hydrocarbon substrate; aliquots (10−20 μL) of the reaction solution were sampled periodically and quenched with excess KI/EtOH, and the liberated I_2 was determined by iodometry. Linear $\ln[(a - x)/(b - x)]$ vs time plots were obtained to over 80% reaction; from these k_2 (M^{-1} s^{-1}) values could be estimated (Table 1). In each case, at least two independent runs were performed and the k_2 values averaged (estimated error ≤±8%).

Acknowledgment. We thank the Ministry of University, Scientific and Technological Research of Italy (MURST 40) and the CNR-Progetto Strategico "Tecnologie Chimiche Innovative" (Rome, Italy) for partial support. Work in Bielefeld was supported by the Deutsche Forschungsgemeinschaft (DFG, Ku 663) and the Fonds der Chemischen Industrie (FCI). Thanks are also due to Dr. R. Mello (University of Valencia, Spain) for performing some of the HRMS analyses. One of us (R.C.) is grateful for hospitality during sabbatical leave spent (November 1995−October 1996) at the Department of Chemistry of Brown University, a most gracious host institution.

Supporting Information Available: ^{1}H NMR ($CDCl_3$, 400 MHz), ^{1}H−^{1}H COSY (300 MHz), {^{1}H}^{13}C NMR (100.5 MHz, $CDCl_3$), and HRMS of diol **5a** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961316L

(33) Kuck, D.; Krause, R. A.; Barth, D. To be published.