(neat) 1769, 1741, 1585, 1434, 1295, 1201, 1100, 1050, 954, 868, 824, 696, 664 cm^{-1}; ^1H NMR (acetone-d_6) δ 9.14 (s, 1 H), 9.01 (d, 1 H, J = 5 Hz), 7.79 (d, 1 H, J = 5 Hz), 3.97 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.1, 164.9, 152.9, 149.7, 138.0, 130.2, 122.3, 53.4.

1-(Phenylsulfonyl)indol-3-yl 4-Carbomethoxy-3-pyridyl Ketone (23). To a magnetically stirred suspension of $AlCl_3$ (4.85 g, 36.4 mmol) in CH_2Cl_2 (100 mL) at 25 °C was added the acid chloride **22** (3.59 g, 18 mmol) in 25 mL of CH_2Cl_2, and the mixture was stirred for 10 min. A solution of **1a** (2.34 g, 9.1 mmol) in CH_2Cl_2 (25 mL) was added dropwise, and the mixture was stirred overnight at 25 °C and quenched with ice. The usual workup and flash chromatography with 1:1 hexane/CH_2Cl_2 gave 1.93 g (50%) of **23** as an amber oil. Crystallization from ether gave the analytical sample as light yellow crystals: mp 146–149 °C; IR (KBr) 1740, 1670, 1545, 1445, 1380, 1290, 1180, 975, 865, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.9–7.0 (m, 13 H), 3.4 (s, 3 H); ^{13}C NMR 188.8, 165.2, 151.8, 148.6, 137.0, 136.9, 135.0, 134.9, 134.6, 133.6, 129.6, 127.2, 127.0, 126.2, 125.1, 123.1, 122.9, 121.7, 113.0, 52.8; mass spectrum, m/e 420, 284, 236, 220, 164, 141, 115, 77 (100); UV (95% EtOH) λ_{max} 222 nm, 263 (sh), 268 (sh), 277 (sh), 280.

Anal. Calcd for $C_{22}H_{16}N_2O_5S$: C, 62.85; H, 3.84; N, 6.66; S, 7.63. Found: C, 62.79; H, 3.86; N, 6.65; S, 7.55.

6*H*-Pyrido[4,3-*b*]carbazole-5,11-quinone (24). To a magnetically stirred solution of the keto ester **23** (0.461 g, 1.1 mmol) in dry THF (50 mL) at −75 °C was slowly added via cannula a solution of the lithium salt of *N,N,N'*-trimethylethylenediamine (1.2 mmol) prepared as described earlier in 25 mL of dry THF. The resulting light orange solution was stirred at −75 °C for 2 h, and a solution of lithium bis(trimethylsilyl)amide (1.25 mmol) in THF (50 mL) was added via cannula and the mixture was stirred overnight under N_2. The solvent was removed in vacuo, saturated aqueous $NaHCO_3$ (100 mL) was added, and the mixture was extracted with ethyl acetate. The usual workup and flash chromatography using initially 1:1 hexane/CH_2Cl_2 and then 1:1 hexane/ethyl acetate gave 0.129 (47%) of **24**: mp 345–347 °C dec (lit.[19] mp 317–320 °C). This sample was identical (TLC, IR, mass spectrum) with a sample kindly provided by Professor J. A. Joule.

Acknowledgment. This investigation was supported by PHS Grant GM-30761 awarded by the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, Grant CH-200B from the American Cancer Society, and Merck Sharp and Dohme Research Laboratories. We also thank Professor John A. Joule for samples and spectra of **20** and **24** and Dr. Timothy C. Barden for obtaining some of the spectra.

Photocyclization of *o*-Halostilbenes

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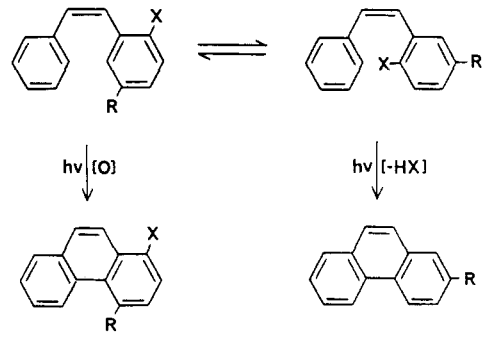
The photocyclization reactions of several ortho-halogenated stilbene derivatives were examined under both oxidative conditions (iodine/cyclohexane) and basic conditions (sodium methoxide/methanol). The major products were those anticipated from photodehydrogenation and photodehydrohalogenation, respectively. In some cases photodebromination of the product occurred. Some regiochemical control in phenanthrene synthesis can be achieved as is illustrated by a synthesis of dehydroorchinol acetate.

Since its discovery more than three decades ago[1] the photocyclization of stilbene derivatives has become a standard method for the preparation of phenanthrenes.[2,3] The yields are generally good and the preparation of the necessary stilbenes is typically straightforward. While the reaction is usually carried out under oxidative conditions, some interesting variations are known, including the photolysis of stilbenes with halogen in an ortho position. These substituents have been used as blocking groups in oxidative photolyses[4] and have been removed in photodehydrohalogenations[5] (Scheme I).

This scheme offers the potential for regiochemical control in the photolysis of stilbenes with meta substituents (Scheme I, R ≠ H). These generally photocyclize with little selectivity giving mixtures of 2- and 4-substituted phenanthrenes.[6] To date, no comparative study has been published in which the photochemistry of *o*-halostilbenes is examined under both oxidative and nonoxidative (i.e., basic) conditions. We wish to report the results of such a study.

Scheme I



Results

Stilbenes **1a–d** and the naphthyl compounds **4a** and **4b** were prepared by Wittig reactions (Experimental Section),

(1) (a) Parker, C. O.; Spoerri, P. E. *Nature (London)* **1950**, *166*, 603. (b) Buckles, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 1040.
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(3) Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 1.
(4) See, for example: Mervič, M.; Ghera, E. *J. Org. Chem.* **1980**, *45*, 4720.
(5) Examples include: (a) Cava, M. P.; Mitchell, M. J.; Havlicek, S. C.; Lindert, A.; Spangler, R. J. *J. Org. Chem.* **1970**, *35*, 175. (b) Cava, M. P., Stern, P.; Wakisaka, K. *Tetrahedron* **1973**, *29*, 2245. (c) Cava, M. P.; Libsch, S. S. *J. Org. Chem.* **1974**, *39*, 577. (d) Castedo, L.; Saa, C.; Saa, J. M.; Suau, R. *J. Org. Chem.* **1982**, *47*, 513.
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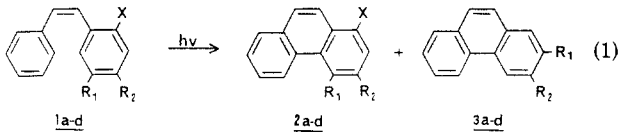
0022-3263/85/1950-5457$01.50/0

Table I

stilbene	X	R_1	R_2	conditions	2, %	3, %	product ratio
1a	Cl	CH_3	H	oxidative	95	0	>20
				basic	8	31	4.0
1b	Br	CH_3	H	oxidative	65[a]	0	>20
				basic	16[b]	20	1.3
1c	Br	OCH_3	H	oxidative	71[c]	7	10
				basic	10	41	4.1
1d	Br	OCH_2O		oxidative	63	12	5.3
				basic	0	57	>20

[a] Includes 22% dehalogenated product. [b] Includes 13% dehalogenated product. [c] Prolonged irradiation resulted in the formation of dehalogenated product.

and their photocyclization reactions were examined. Compounds **1a–d** were chosen as examples whose parents (X = H) show little if any selectivity in their photocyclization reactions.[6-8] They were irradiated under standard oxidative conditions (cyclohexane/iodine) as well as under basic conditions (sodium methoxide/methanol). A Vycor filtered 450-W medium-pressure mercury vapor lamp was used. The major products were those anticipated from cyclodehydrogenation and cyclodehydrohalogenation, respectively. Products **3a–d** were known compounds; compounds **2a,c,d** were characterized by ^1H NMR and IR spectroscopy and by elemental analysis (Experimental Section). Particularly useful were three aspects of the ^1H NMR spectra: (1) the chemical shifts of the methyl or methylene singlets in the bay region areas of **2a–d** are deshielded relative to the same groups in **3a–d**, (2) only one phenanthrene bay region proton (C-5) is present, and its chemical shift is strongly influenced by the nature of the substituent at C-4, for example, being strongly deshielded by the oxygen atoms in **2c** and **2d**,[8] and (3) the presence of a characteristic doublet at ca. 8 ppm due to the C-10 proton which is deshielded by the halogen peri to it. Results are presented in eq 1 and Table I. Yields and product ratios were determined by ^1H NMR spectroscopy.

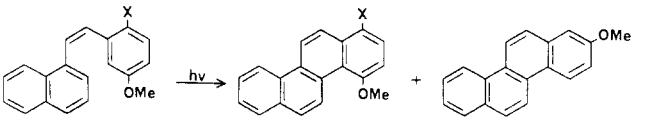


1a-d 2a-d 3a-d (1)

The total yields are typical of those reported for stilbene photocyclizations,[2,3] the yields under oxidative conditions were consistently higher than those under basic conditions. The product ratios were variable, but in all cases except one were at least 4; thus a substantial degree of regiochemical control may be achieved. The formation of oxidative products under basic conditions can be attributed to the presence of adventitious oxidants and is frequently observed.[3]

Photodehalogenation was occasionally a problem, especially with bromo compound **1b**. In oxidative photolyses, the yield of 4-methylphenanthrene ranged from 24% to 50% of the total product depending on the irradiation time. Interestingly, very little 2-methylphenanthrene was detected. Since 3-methylstilbene gives nearly equal amounts of 2- and 4-methylphenanthrene,[6] this observation indicates that dehalogenation is a secondary reaction occurring after photocyclization. No dehalogenation was observed with the corresponding chloro compound **1a**. Reduction of the **1b** photoproduct mixture with $LiAlH_4$[9] afforded 4-methylphenanthrene in an overall yield of 65% from stilbene **1b**, so the two-step sequence of oxidative photocyclization followed by reduction constitutes an efficient, regioselective route to the 4-substituted derivative.

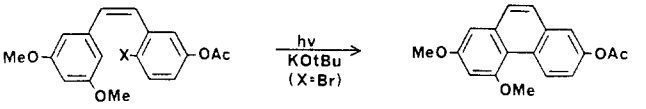
Next, naphthyl compounds **4a** and **4b** were examined. The parent compound (**4a**) shows approximately 3:1 selectivity favoring cyclization ortho to the methoxy group.



4a, X=H
b, X=Br 5a,b 6

We were interested in determining whether this selectivity could be reversed by the introduction of an ortho bromine. Under oxidative conditions the selectivity increased to approximately 10:1; however, dehalogenation again proved troublesome. Products **5a** and **5b** were consistently formed in nearly equal amounts. Reduction of the mixture with $LiAlH_4$ afforded **5a** in an overall 72% yield from **4b**. Under basic conditions the ratio of **5a,b** to **6** was reduced to 1.3:1 but was not reversed.

Finally, the above results were sufficiently encouraging to prompt us to apply the method to a regiocontrolled synthesis of dehydroorchinol acetate (**8**), a precursor to the fungicidal phytoalexin orchinol. Photocyclization of stilbene **7b** in *t*-BuOH/KO-*t*-Bu afforded **8** in a 60% yield; no other photocyclized products could be detected by ^1H NMR spectroscopy. This constitutes a significant improvement on the synthesis reported by Stoessl et al.,[10] in which photolysis of **7a** gave a nearly 1:1 mixture of products, and the synthesis described by Letcher and Wong,[11] which gave a 4:1 mixture of products starting with the 2-iodo-3-acetoxy derivative.



7a, X=H
b, X=Br 8

In summary, considerable control can be achieved in the direction of cyclization of *o*-halostilbenes, particularly those derived from parents which themselves show little selectivity. Photodebromination is often an interfering side reaction; however, the sequence of oxidative photocyclization followed by dehalogenation is still an efficient route to 4-substituted phenanthrene derivatives.

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Experimental Section

NMR spectra were recorded on a Varian T-60 spectrometer with Me_4Si as an internal standard. IR spectra were recorded on either a Perkin-Elmer Model 457 or Model 1320 spectrophotometer. All solvents were fractionally distilled and stored over molecular sieves prior to use. Melting points are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Stilbenes—General Procedure. A stirred mixture of phosphonium salt (1.8 mmol) and aldehyde (1.8 mmol) in 20 mL of DMF was heated to 80 °C, and sodium methoxide (2.0 mmol) in methanol (5 mL) was added in one portion. Stirring at 80–90 °C was continued for 1 h, after which the mixture was cooled and poured into an equal volume of water. The resulting mixture was extracted with chloroform, and the extracts were washed with water and dried ($MgSO_4$). After evaporation of the solvents the stilbenes were isolated by column chromatography (alumina, 0–5% ether/petroleum ether). Yields are given for mixtures of cis and trans isomers. For compounds **1a–d** and **4a** the trans isomer was purified and characterized. For compound **4b**, the mixture of isomers was characterized. In all cases the cis/trans mixture was used for the photochemical experiments. In the syntheses of **4a** and **4b**, residual 1-naphthaldehyde was removed by treatment with Girard's "T" Reagent.[12]

1a: 44% yield; oil; ^1H NMR (CCl_4) δ 2.35 (s, 3 H), 6.8–7.7 (m, 10 H); IR (neat) 690, 740, 770, 800, 955, 1040, 1465, 2930, 3030 cm^{-1}. Anal. Calcd for $C_{15}H_{13}Cl$; C, 78.77; H, 5.73. Found: C, 78.46; H, 5.64.

1b: 67% yield; oil; ^1H NMR (CCl_4) δ 2.33 (s, 3 H), 6.7–7.6 (m, 10 H); IR (neat) 688, 754, 781, 802, 959, 1023, 1465, 2920, 3030 cm^{-1}. Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80. Found: C, 65.72; H, 4.75.

1c: 83% yield; mp (EtOH) 63–64 °C; ^1H NMR (CCl_4) δ 3.69 (s, 3 H), 6.5–6.9 (m, 1 H), 7.1–7.7 (m, 9 H); IR (CCl_4) 690, 745, 795, 955, 1010, 1280, 1458, 1585, 2940, 3020 cm^{-1}. Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53. Found: C, 62.20; H, 4.67.

1d: 92% yield; mp (EtOH) 83–84 °C; ^1H NMR (CCl_4) δ 5.83 (s, 2 H), 6.4–7.5 (m, 9 H); IR (neat) 760, 1048, 1249, 1477, 1508, 2910, 3020 cm^{-1}. Anal. Calcd for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66. Found: C, 59.14; H, 3.91.

4a: 56% yield; mp (EtOH) 45–47 °C; ^1H NMR (CCl_4) δ 3.73 (s, 3 H), 6.3–8.1 (m, 13 H); IR (neat) 690, 770, 960, 1050, 1155, 1265, 1575, 1595, 2840, 2960, 3060 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.48; H, 6.31.

4b: 42% yield; oil; ^1H NMR (CCl_4) δ 2.98, 3.82 (2 s, combined 3 H), 6.2–8.1 (m, 12 H); IR 765, 785, 1010, 1235, 1285, 1460, 1565, 1590, 2830, 2950, 3050 cm^{-1}; Anal. Calcd for $C_{19}H_{15}BrO$: C, 67.27; H, 4.46. Found: C, 67.62; H, 4.58.

Oxidative Photolyses—General Procedure. A solution of 1 mmol of stilbene and 2 mmol of iodine in 550 mL of cyclohexane was purged with nitrogen for 30 min and irradiated with a 450-W medium-pressure mercury vapor lamp in a quartz immersion apparatus fitted with a Vycor filter. After the irradiation, the cyclohexane was removed by rotary evaporation and the product mixture isolated by column chromatography (alumina, 0–5% ether/petroleum ether). Further purification was accomplished by careful column chromatography and/or crystallization.

1a. Photolysis for 9 h (100% conversion) gave a 95% yield of **2a**: oil; ^1H NMR (CCl_4) δ 2.88 (s, 3 H), 7.09 (d, J = 8 Hz, 1 H), 7.3–7.8 (m, 5 H), 8.11 (d, J = 9 Hz, 1 H), 8.5–8.7 (m, 1 H); IR (neat) 748, 813, 1095, 1124, 1377, 2880, 2980, 3050 cm^{-1}. Anal. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89. Found: C, 79.80; H, 5.00.

1b. Photolysis for 6 h (100% conversion) gave a mixture containing 22% 4-methylphenanthrene and 43% **2b**. Several attempts to obtain an analytically pure sample of **2b** by recrystallization and column chromatography were unsuccessful. However, the following ^1H NMR data obtained from an impure sample are consistent with the proposed structure: δ (CCl_4) 2.92 (s, 3 H), 7.05 (d, J = 8 Hz, 1 H), 7.2–7.8 (m, 5 H), 8.23 (d, J = 9 Hz, 1 H), 8.4–8.8 (m, 1 H). Reduction of this mixture using the procedure of Brown et al. ($LiAlH_4$, THF, 65 °C)[9] gave essentially a quantitative yield of 4-methylphenanthrene, identified by spectroscopic comparison with an authentic sample.[6]

1c. Photolysis for 5 h (60% conversion) gave a 71% yield of **2c**: mp (MeOH) 99–100 °C; ^1H NMR (CCl_4) δ 4.00 (s, 3 H), 6.73 (d, J = 9 Hz, 1 H), 7.3–7.8 (m, 5 H), 8.13 (d, J = 9 Hz, 1 H), 9.3–9.6 (m, 1 H); IR (CCl_4) 750, 817, 1075, 1242, 2840, 2940, 3055 cm^{-1}. Anal. Calcd for $C_{15}H_{11}BrO$: C, 62.74; H, 3.87. Found: C, 62.90; H, 4.01 [and approximately a 7% yield of **3c**, mp 97–98 °C (lit. mp 96–97 °C[13])].

1d. Photolysis for 3 h (100% conversion) gave a mixture consisting of a 63% yield of **2d**: mp (EtOH) 114–115 °C; ^1H NMR (CCl_4) δ 6.03 (s, 2 H), 6.8–7.6 (m, 5 H), 7.82 (d, J = 9 Hz, 1 H), 8.7–8.9 (m, 1 H); IR (CCl_4) 742, 801, 1050, 1104, 1277, 1439, 2890, 3060 cm^{-1}. Anal. Calcd for $C_{15}H_9BrO_2$: C, 59.82, H, 3.01. Found: C, 60.05; H, 2.97 [and a 12% yield of **3d**, mp 93–95 °C (lit. mp 93–95 °C[14])].

4a. Photolysis for 5 h (100% conversion) gave a mixture consisting of a 33% yield of 4-methoxychrysene (**5a**), mp 102–104 °C (lit. mp 102–103 °C[15]), and an 11% yield of 2-methoxychrysene (**6**), mp 251–252 °C (lit. mp 250–251 °C[16]).

4b. Photolysis for 4 h (100% conversion) gave a 50% yield of **5b**: mp 123–125 °C; ^1H NMR ($CDCl_3$) δ 4.12 (s, 3 H), 7.02 (d, J = 9 Hz, 1 H), 7.3–8.2 (m, 5 H), 8.45 (d, J = 10 Hz, 1 H), 8.7–9.0 (m, 2 H), 9.75 (d, J = 9 Hz, 1 H); IR (CCl_4) 745, 815, 1060, 1100, 1255, 1320, 1400, 2830, 2930, 3050 cm^{-1}. A 39% yield of **5a** and a small amount (ca. 4%) of **6** were also obtained. Reduction of the product mixture with $LiAlH_4/THF$[9] gave 4-methoxychrysene in an overall 72% yield from **4b**.

Basic Photolyses—General Procedure. A solution of 1 mmol of stilbene and 2 mmol of sodium methoxide in 550 mL of methanol was purged for 30 min, and the solution was irradiated as described above. After the irradiation the methanol was evaporated, water added, and the resulting mixture extracted with chloroform. The chloroform extracts were dried ($MgSO_4$) and evaporated and the products isolated as described above.

1a. Photolysis for 7 h (92% conversion) gave a 31% yield of **3a**, identified by spectroscopic comparison with an authentic sample, and an 8% yield of **2a**.

1b. Photolysis for 6 h (94% conversion) gave a mixture which was found by ^1H NMR analysis to contain ca. 3% **2b**, 13% 4-methylphenanthrene, and 20% 2-methylphenanthrene.

1c. Photolysis for 6 h (100% conversion) gave a 41% yield of **3c** and a 10% yield of **2c**.

1d. Photolysis for 8 h (100% conversion) gave a 57% yield of **3d**.

4b. Photolysis for 5 h (100% conversion) gave a mixture which was found by ^1H NMR analysis to contain 7% **5a**, 42% **5b**, and 38% **6**.

Dehydroorchinol Acetate (8). A solution of 0.18 g of stilbene **7b** (prepared from 2-bromo-5-hydroxybenzaldehyde and (3,5-dimethoxybenzyl)triphenylphosphonium bromide[10]) and 0.15 g of potassium *tert*-butoxide in a mixture of 18 mL of *tert*-butyl alcohol and 2 mL of benzene was placed in two quartz tubes, purged with nitrogen for 30 min, placed 5 cm from the immersion well apparatus described above, and irradiated for 6 h. The solvents were evaporated, and the resulting mixture was partitioned between chloroform and 5% HCl. The chloroform was dried ($MgSO_4$), a few drops of acetic anhydride was added, and the solvent was evaporated. NMR analysis showed 77% conversion to a single photoproduct, which was isolated by preparative TLC (silica gel/benzene eluent) and crystallized from methanol (60% yield based on starting material consumed): mp 155–156 °C (lit. mp 154–156 °C[17]); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.90 (s, 3 H), 4.05 (s, 3 H), 6.7–7.7 (m, 6 H), 8.68 (d, J = 10 Hz, 1 H).

Acknowledgment. Financial support provided by the Haines Research Fund is gratefully acknowledged.

Registry No. (*Z*)-**1a**, 99398-09-1; (*E*)-**1a**, 99398-19-3; (*Z*)-**1b**, 99398-10-4; (*E*)-**1b**, 99398-20-6; (*Z*)-**1c**, 99398-11-5; (*E*)-**1c**,

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99398-21-7; (Z)-**1d**, 99398-12-6; (E)-**1d**, 99398-22-8; **2a**, 15248-05-2; **2b**, 99398-13-7; **2c**, 99398-14-8; **2d**, 99398-15-9; **3a**, 2531-84-2; **3c**, 13837-48-4; **3d**, 224-09-9; (Z)-**4a**, 99398-16-0; (E)-**4a**, 22920-31-6; (Z)-**4b**, 99398-17-1; (E)-**4b**, 99398-23-9; **5a**, 63020-59-7; **5b**, 99398-18-2; **6**, 63020-58-6; **7b**, 54901-08-5; **8**, 42123-39-7; 4-methylphenanthrene, 832-64-4; 2-bromo-5-hydroxybenzaldehyde, 2973-80-0; (3,5-dimethoxybenzyl)triphenylphosphonium bromide, 24131-30-4.

Synthesis of Biological Markers in Fossil Fuels. 4.[1] C_{27}, C_{28}, and C_{29} 13β,17α(*H*)-Diasteranes

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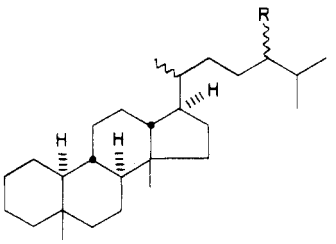
The rearrangement of 5-cholestene to (20ξ)-13(17)-diacholestenes, separation of C-20 epimers, and further reduction provided an unambiguous synthesis of the biomarkers (20*R*)- and (20*S*)-13β,17α(*H*)-diacholestanes. Repetition of this sequence using (24*R*)-5-campestene or (24*R*)-5-stigmastene provided the analogous C_{28} and C_{29} diasteranes.

The diagenesis[3] of petroleum from sedimentary organic matter results in the reduction and rearrangement of common sterols to a variety of geosteranes.[3] Although these geosteranes commonly appear in parts per million ratios in petroleum deposits, the advent of modern gas chromatography–mass spectrometry permits the identification and quantitation of these geosteranes. These compounds that Eglinton[4] defined as "biomarkers" embrace an array of structural types including the traditional C_{27}, C_{28}, and C_{29} steroid skeletons, various aromatized steranes, and rearranged steranes such as the diasteranes **1**.



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In recent years, this knowledge was utilized to provide valuable information for the petroleum explorationist interested in the source, maturation, and migration of crude oils.[5] As a consequence, considerable interest developed in the precise structure of certain uncommon isomerized or rearranged geosteranes particularly with regard to stereochemistry. The rearranged geosteranes were of particular interest since they undergo biodegradation at a slower rate than normal steranes and thus appear even in heavily biodegraded crude oils.[6] Although mass spectral fragmentation patterns defined certain stereochemical parameters, the availability of authentic samples would eliminate any ambiguity and would place the GC–MS identification on a secure footing.

The diasteranes **1** comprise a group of "backbone rearrangement" products of the normal sterane skeleton that were first identified by Blunt, Hartshorn, and Kirk[7] in the acid-catalyzed rearrangement of cholest-4-ene or cholest-5-ene (**3a**). These chemical curiosities were subsequently identified in an immature shale from Jouy-aux-Arches, France. Albrecht[8] also established that a naturally occurring mineral, montmorillonite, would also trigger the rearrangement process of unsaturated normal steranes and coined the term "diasteranes" to describe this family of geosteranes arising from the diagenesis of steranes. Both Albrecht[9] and Jacquesy[10] reported independent syntheses of various diasterane stereoisomers.

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