chemical correlations described above.

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Registry No.—**1a,** 50-14-6; **1b,** 65338-41-2; **2a,** 65377-95-9; **2b,** 65338-42-3; **7,** 65338-43-4; **8,** 65338-44-5; benzoyl chloride, 98-88-4; Ts-Cl, 98-59-9.

Supplementary Material Available: Table II giving the NMR, UV, and/or MS data for the 18 compounds **3–6, 7,** and **8** (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) For Paper 13 in this series, see W. H. Okamura, M. N. Mitra, M. R. Pirio, A. Mouriño, S. C. Carey, and A. W. Norman, *J. Org. Chem.*, **43,** 574 (1978); (b) see paper 12 for a related study of 10,19-dihydrovitamins, W. H. Okamura, M. L. Hammond, A. Rego, A. W. Norman, and R. M. Wing, *J. Org. Chem.*, **42,** 2284 (1977).
(2) This study was supported by USPHS Grant AM-16595 and by a grant from the Intramural Research Fund of the University of California, Riverside.
(3) Spanish Ministry of Education and Science Postdoctoral Fellow.
(4) Vitamin D_3 (cholecalciferol), a prohormone which possesses the C_8H_{17} side chain of cholesterol, is actually the naturally occurring form of vitamin D.
(5) A. Verloop, A. L. Koevoet, and E. Havinga, *Recl. Trav. Chim. Pays-Bas,* **74,** 1125 (1955).
(6) For articles related to the preparation and characterization of the 10,19-dihydrovitamins of the vitamin D_2 series, see: (a) F. von Werder, *Z. Physiol. Chem.*, **260,** 119 (1939); (b) K. Schubert, *Naturwissenschaften,* **41,** 231 (1954); (c) K. Schubert, *Biochem. Z.,* **326,** 132 (1954); (d) K. Schubert, *ibid.,* **327,** 507 (1956); (e) K. Schubert and K. Wehrberger, *ibid.,* **328,** 199 (1956); (f) P. Westerhof and J. A. Keverling Buisman, *Recl. Trav. Chim. Pays-Bas,* **75,** 453 (1956); (g) F. von Werder, *Justus Liebigs Ann. Chem.*, **603,** 15 (1957); (h) P. Westerhof and J. A. Keverling Buisman, *Recl. Trav. Chim. Pays-Bas,* **76,** 679 (1957); (i) P. Westerhof and J. A. Keverling Buisman, *ibid.,* **78,** 659 (1959); (j) L. F. Fieser and M. Fieser, "Steroids", Reinhold, New York, N.Y., 1959, pp 143–6; (k) A. G. M. Barrett, D. H. R. Barton, R. A. Russell, and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1,* 631 (1977).
(7) Commercial dihydrotachysterol$_2$ (**5d**) clearly has the stereostructure shown as determined by comparison of its 300 MHz ^{1}H-NMR spectrum with that of dihydrotachysterol$_3$ (vitamin D_3 side chain) (ref 1b).
(8) The two products (**3d** and **4d**) obtained by saturating the 10,19 double bond of vitamin D_2 have been labeled in our laboratory as DHV$_2$-II and DHV$_2$-III, respectively. Other workers (ref 6e,h,i,k) refer to **4d** as DHV$_2$-IV while our laboratory (see also ref 6g,j) labels **6d,** the C_{10} epimer of dihydrotachysterol$_2$ (**5d**), as DHV$_2$-IV. See footnote 17 of ref 1b. While this study was in progress, Barett et al. (ref 6k) reported the fact that catalytic reduction of **1a** results in only two products: DHV$_2$-II (**3d**) and DHV$_2$-IV (**4d** or what we call DHV$_2$-III).
(9) M. L. Hammond, A. Mouriño, P. Blair, W. Wecksler, R. L. Johnson, A. W. Norman, and W. H. Okamura, "Vitamin D: Biochemical, Chemical and Clinical Aspects Related to Calcium Metabolism", A. W. Norman, K. Schaefer, J. W. Coburn, H. F. DeLuca, D. Fraser, H. G. Grigoleit, and D. v. Herrath, Ed., W. De Gruyter Publisher, Berlin, 1977, pp 1–4.
(10) T. A. Giudici and T. C. Bruice, *J. Org. Chem.*, **35,** 2386 (1970).
(11) It appears that we reversed the **5a–6a** assignments in writing the earlier manuscript (ref 1b). As a result of a double error, the assigned stereochemistries and product ratios as given in ref 1b are correct.
(12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, pp 239 and 288.
(13) For this reason, homogeneity of the various DHV's was established by TLC under several sets of conditions. NMR and high resolution mass spectral data are given in Table II.
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Stereochemical Assignment of (*E*)- and (*Z*)-2-(1-Naphthyl)-1-phenylpropene and Their Photocyclization to 5-Methylchrysene

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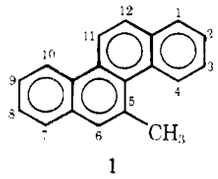
Dehydration of 2-(1-naphthyl)-1-phenyl-2-propanol (**3**) gave varying ratios of (*E*)-2-(1-naphthyl)-1-phenylpropene (**4**), (*Z*)-2-(1-naphthyl)-1-phenylpropene (**5**), and 2-(1-naphthyl)-3-phenylpropene (**6**), depending upon conditions and choice of reagent. Assignment of configuration to these alkenes by UV and ^{1}H NMR spectroscopy was equivocal, but unambiguous assignment was made through comparison of chemical shifts in the ^{1}H NMR spectra of the cis diols and the corresponding cyclic phenylboronates prepared from **4** and **5**. Photocyclization of **4** or **5** gave 5-methylchrysene (**1**), whereas **6** was inert.

The environmental carcinogen 5-methylchrysene (**1**), which occurs in the biologically active neutral subfractions of tobacco smoke, is more carcinogenic on mouse skin than any of the other monomethylchrysene isomers or chrysene itself.[2] The carcinogenic activity of **1** is comparable to that of benzo[*a*]pyrene.[3] 5-Methylchrysene is also more mutagenic towards *S. typhimurium* than the other monomethylchrysenes.[4]

Previous syntheses[2a,5] of **1** involved multistep routes and gave low yields, none exceeding 5%. In order to continue carcinogenicity studies of **1**, a more efficient synthesis was needed. Photocyclization of the appropriately substituted alkene[6] appeared to be a more suitable route. We now report a shorter and improved synthesis (20% yield) of **1** via UV irradiation of (*E*)- or (*Z*)-2-(1-naphthyl)-1-phenylpropene (**4** and **5**, respectively) in the presence of iodine and oxygen as shown in Scheme I.



1

Treatment of 1-acetonaphthone with benzylmagnesium chloride gave **3** in 75% yield. Dehydration of **3** was performed under a variety of conditions in an attempt to control the ratio of the resulting alkenes.[7] In all cases, GC analyses[8] indicated the three products shown in Table I.

During dehydration of **3** in refluxing benzene with Amberlyst-15 (A-15) resin,[9] the ratio of alkenes **4/5/6** (48:9:43) remained fairly constant while alcohol **3** was still present. After **3** was consumed, the concentration of exo alkene **6** decreased rapidly with simultaneous increase of **4** to a maximum of 57%. Alkene **4** then slowly diminished as the concentration of **5** increased. After 36 h, the ratio **4/5/6** (54:45:1)[10] stabilized

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Table I. Acid-Catalyzed Dehydration of 3

Reagent and temp (°C)	Ratio of Alkenes 4	5	6
Amberlyst-15, C_6H_6 (80)	48[a]	9	43
	57[b]	30	13
	54[c]	45	1
Trifluoracetic acid (27)	83[d]	16	1
$POCl_3$, pyridine (0)	33[e]	5	62

[a] During dehydration of **3**. [b] 2.5 h after disappearance of **3**. [c] 36 h after disappearance of **3**. [d] 0.5 h. [e] No change over 3 h.

and the concentration of **4** was only slightly favored. The kinetic formation of **4** and **6**, particularly with trifluoroacetic acid, can be rationalized by examination of the presumably most stable conformation of the alcohol **3** and the resulting cation shown in Scheme II.

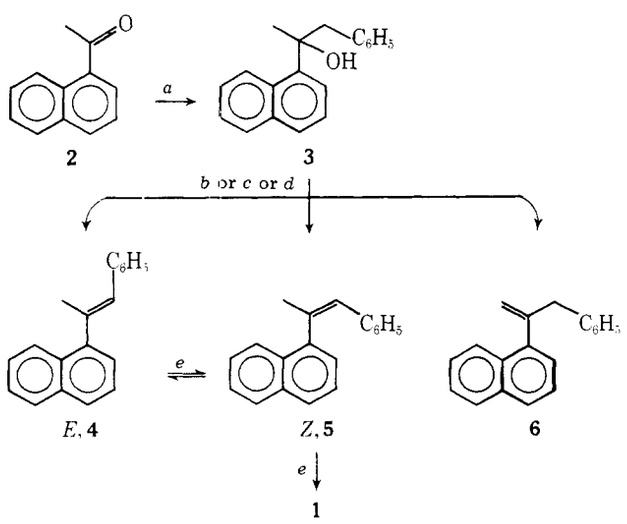
In the preferred conformation of alcohol **3**, the phenyl and naphthyl groups are anti. Protonation of the hydroxyl followed by loss of water generates the cation which has two protons H_a and H_b correctly oriented for periplanar elimination[11] to **4** or **6**.

The failure of the *E* alkene **4** to predominate to any great extent over the *Z* alkene **5** after prolonged exposure to equilibrating conditions should be noted. Although both **4** and **5** exhibit a steric interaction between the methyl group and the naphthalene *peri*-hydrogen,[12] the net result is to reduce the usual difference in stability between *E* and *Z* isomers.

Under nonequilibrating conditions, the dehydration of **3** using phosphorus oxychloride and excess pyridine at 0 °C favored formation of **6** (**4**/**5**/**6**; 6:1:12). This ratio did not change over 3 h at 0 °C. The preponderance of the thermodynamically less stable alkene **6** may be related to the ease of approach of base preceding elimination.[11]

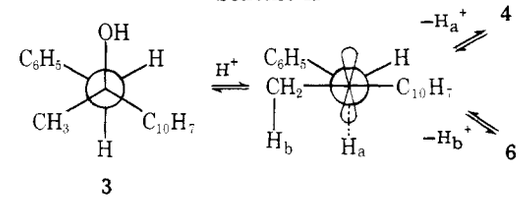
The alkenes **4**, **5**, and **6** were separated via picric acid with the picrate of **4**, mp 94–95 °C, being the least soluble and most stable. Successive concentrations of the mother liquor gave the picrate of **6**, which is less stable and dissociated on attempted recrystallization from ethanol. The *Z* alkene **5** did not form a picrate under these conditions and was isolated from the mother liquor. Dreiding models and NMR data, subsequently to be discussed, show that the naphthyl ring of the *Z* isomer of **5** is crowded (aryl–aryl interaction) compared to that of **4**. This may explain the decreased stability of the picrate of **5**.

Scheme I



[a] $C_6H_5CH_2MgCl$. [b] A-15, C_6H_6, Δ. [c] CF_3CO_2H. [d] $POCl_3$, pyridine. [e] *hν*, I_2, O_2, C_6H_6.

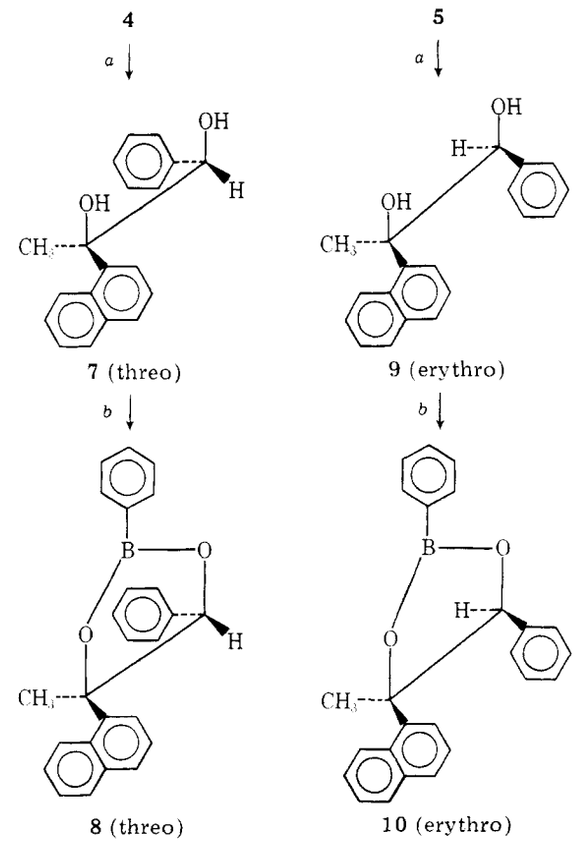
Scheme II



Attempts to assign configuration to the *E* and *Z* alkenes **4** and **5** using ^1H NMR and UV spectroscopy led to uncertain results. However, the assignment of configuration to **4** and **5** was achieved through ^1H-NMR studies of the diol and the phenylboronate derivatives of these alkenes.[13] The *threo*-2-(1-naphthyl)-1-phenylpropane-1,2-diol (**7**) was prepared by treatment of the *E* alkene **4** with osmium tetroxide and hydrolysis of the osmate with sodium sulfite. Analogously, the *Z* alkene **5** gave the erythro diol **9**. Treatment of each of these diols (**7** and **9**) with phenylboronic acid gave the corresponding cyclic phenylboronates **8** and **10** respectively, as shown in Scheme III. The configurations used in Scheme III are an arbitrary selection for **7**, **8**, **9**, and **10** and should not be considered as an absolute assignment.[14]

Assignments have previously been made for meso and racemic aryl containing diols[15] and their corresponding phenylboronates[13] based on chemical shifts in the ^1H-NMR spectra produced by anisotropic effects of the aromatic ring cis to a methyl group. The ^1H-NMR spectra of the phenylboronates have the advantage of showing enhanced methyl proton shifts relative to what is observed for the diols. Thus, this technique allows stereochemical assignment to *E* and *Z* alkenes **4** and **5**, whereas other methods (NMR and UV) applied to these isomers failed to give unambiguous assignments. The ^1H-NMR data of the diols and phenylboronates are presented in

Scheme III



[a] OsO_4, pyridine, Et_2O; Na_2SO_3. [b] $C_6H_5B(OH)_2$.

Table II. ^{1}H NMR (δ) Data for Diols 7 and 9 and Phenylboronates 8 and 10

	Registry no.	Aromatic H	CH_3	H(C-1)	OH(C-1)	OH(C-2)
Threo diol (7)	65059-19-0	6.72–8.86	1.40	3.22	3.20	5.46
Erythro diol (9)	65059-20-3	7.00–8.80	1.66	2.38	2.28	5.34
Threo boronate (8)	65059-21-4	7.34–8.28	1.62	6.02		
Erythro boronate (10)	65059-22-5	6.70–8.20	2.10	5.88		

Table III. UV and ^{1}H-NMR (δ) Data of Alkenes 4, 5, and 6

	4[e]	5[f]	6[g]
UV (EtOH), nm	222.5 (4.79)	225 (4.87)	225 (4.77)
(log ϵ)	245[a] (4.15)	245[a] (4.28)	*b*
	282.5 (4.04)	285 (3.98)	282.5 (3.85)
^{1}H NMR (CCl_4)			
CH_3	2.30 (d, J = 1 Hz, 3)	2.24 (d, J = 1 Hz, 3)	CH_2 3.68 (s, 2)
Vinyl **H**	6.52 (s, 1)[c]	*d*	5.08 (d, J = 2 Hz, 1) 5.22 (d, J = 2 Hz, 1),
Aromatic **H**	7.00–8.02 (m, 12)	6.64–7.88 (m, 13)[d]	6.94–8.02 (m, 12)

[a] Shoulder. [b] No shoulder at 245. [c] Broad, but no discernible splitting. [d] The vinyl proton signal was buried within the aromatic proton resonances. [e] Registry no. 65059-23-6. [f] Registry no. 65085-71-4. [g] Registry no. 65059-24-7.

Table II. Infrared studies have also been used to establish the relative configuration of vicinal diols.[16]

In making the configurational assignments for the threo isomers relative to the erythro isomers (diols as well as the corresponding phenylboronates), the methyl proton resonances would be expected to appear at higher field because they lie within the shielding region of the phenyl ring.[13,15] The hydroxyl protons (in threo diol **7**) should absorb at lower field because of an increased intramolecular hydrogen bonding, which decreases electron density on oxygen and deshields the hydroxyl protons.[15] The benzylic protons are deshielded in the threo isomers **7** and **8** relative to those of the erythro isomers **9** and **10** and opposite to that which is generally observed.[17] This effect may result from interaction of the methyl group with the *peri*-hydrogen of the naphthyl ring which causes rotation of the naphthyl ring and in turn deshielding of the benzylic proton in the threo isomers. In summary, these directional shifts are consistently observed in the spectra of the diol and phenylboronate derived from the *E* alkene, mp 36–37 °C. This allows assignment of stereochemistry to the diols **7** and **9**, mp 102–104 and 109–110.5 °C, respectively, which in turn allows structural assignment of *E* and *Z* alkenes **4** and **5**.

Attention is directed to this use of phenylboronic acid. Addition of an equimolar quantity of phenylboronic acid to a deuteriochloroform solution of **7** or **9** followed by 10 min of shaking and filtration through glass wool to remove water gave quantitative conversion to the cyclic phenylboronates **8** and **10**. The locked orientation of substituents on these cyclic esters leads to enhanced chemical shifts in the ^{1}H-NMR spectra that are valuable for making diol configuration assignments.[13]

Considering the above stereochemical assignments, it is of interest to examine the ^{1}H-NMR and UV data obtained for **4**, **5**, and **6**. The structure of the latter is conclusively established through the ^{1}H-NMR spectrum, which shows vinyl protons at δ 5.21 (broad d, J = 2 Hz) and δ 5.08 (d, J = 2 Hz) and two benzylic protons at δ 3.68 (s) as shown in Table III.

The similarity of the UV data from **4**, **5**, and **6** precluded satisfactory use as stated above in making structural assignments.[18] The similarities in the UV spectra of **4** and **5** result from steric interaction, as previously mentioned, between the *peri*-hydrogen of the naphthyl ring and the methyl group,[12] thus preventing coplanarity in the *E* as well as the *Z* isomer.

The ^{1}H-NMR data of **4** and **5** are unusual in that the vinyl proton resonance of the *E* isomer **4** appears at higher field than that of the *Z* isomer **5**. Generally in 1,2-diarylethenes, these resonance positions are reversed, although exceptions are known.[19] The usual occurrence of vinyl protons at lower field in *E* isomers is attributed to the coplanarity of the aromatic ring and double bond.[19] This places the vinyl proton in the deshielding region of the aromatic ring. The nonplanarity of the naphthyl ring and alkene double bond in **4** causes the vinyl proton to lie above the naphthyl ring, i.e., in the shielding region, and hence its shift to higher field.[18] Some indication of the angle between the naphthyl ring and the alkene double bond may be seen in the shift of the naphthyl peri proton signal proximal to the methyl group, since an increased angle should lead to an upfield shift due to shielding by the double bond.[12] In **4**, **5**, **6**, and **1**, this appears as a discernible multiplet at δ 7.96, 7.90, 8.02, and 8.90, respectively. The assignments of **4** and **5** are further confirmed by the strong upfield shift of aromatic protons in the *Z* alkene **5**, which is caused by the proximity of aromatic rings.[18]

Photocyclization of **4**, **5**, and **6** with periodic sampling and GC analysis[8] was conducted by irradiation of an air-saturated 0.01 M benzene solution of alkene containing iodine (0.001 M) at 3600 Å. After 7 h, the exo alkene **6** had failed to isomerize or cyclize and was recovered unchanged. No other products were detected by GC. The *E* and *Z* alkenes **4** and **5** both rapidly equilibrated to a fairly constant *E*/*Z* (**4**/**5**, 1:2–3) ratio but the formation of 5-methylchrysene (**1**) was initially faster as shown in Figure 1 when the *Z* alkene was used as starting material. The photocyclization of **4** and **5** is assumed to proceed by a mechanism similar to that for the photocyclization of stilbene.[20]

Preparative-scale photocyclization of **4** and **5** was most conveniently carried out on the mixture of alkenes obtained from acid-catalyzed dehydration. Attempts to increase the yield (29%) by using cupric chloride[21] or using a higher concentration of oxygen were unsuccessful and actually led to decreased yields. Dilution of the benzene solution of alkenes from 0.01 to 0.0025 M also failed to give a significant increase in yield.

The structure of the product from photocyclization was identified as 5-methylchrysene (**1**) by mp 117–117.5 °C (lit.[2a,5] mp 117 °C), mass spectrum,[2a] and ^{1}H NMR.[2a]

Experimental Section[22]

2-(1-Naphthyl)-1-phenyl-2-propanol (3). To the Grignard reagent prepared from 48.6 g (2.0 mol) of magnesium and 252 g (2.0 mol) of benzyl chloride in 500 mL of ether was added a solution of 314 g (1.85 mol) of purified 1-acetonaphthone (**2**) in 500 mL of ether at a rate sufficient to maintain reflux. The mixture was then heated at reflux an additional 0.5 h, cooled, treated with dilute hydrochloric acid, and then ether extracted. The ether extracts were washed with sodium bicarbonate solution, dried ($MgSO_4$), filtered, and concentrated. Recrystallization from a mixture of isohexane[22c] and benzene gave 365 g (75%) of **3**: mp 74–85 °C dec; IR (KBr) 3150 (s), 800 (s), 740 (s), 700 (s), 695 (s), 680 cm^{-1} (s); ^{1}H NMR (CCl_4) δ 2.72 (s, 3, CH_3), 2.80 (s, 1, OH), 3.34, 3.66 (d of d, 2, $J_{HH'}$ = 13 Hz), 6.76–8.80 (m, 12, ArH); MS *m/e* (rel intensity) M^+ 262 (1), 172 (12), 171 (100), 127 (12),

91 (16), 43 (78). Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 87.00; H, 7.06.

Dehydration of 3 to (*E*)-2-(1-Naphthyl)-1-phenylpropene (4), (*Z*)-2-(1-Naphthyl)-1-phenylpropene (5), and 2-(1-Naphthyl)-3-phenylpropene (6). A. To a magnetically stirred flask containing 500 mL of benzene fitted with a Dean-Stark trap were added 50 g (0.191 mol) of **3** and 1 g of A-15 resin.[9] The mixture was heated at reflux temperature until **3** disappeared as shown by GC.[8] Filtration to remove resin, followed by distillation at 140–170 °C (0.3 mm), gave 39.3 g (84%) of alkenes **4/5/6** (2.5:1:2). Equilibration of the alkenes was carried out under similar conditions.

B. To 120 mL of trifluoroacetic acid was added 12.0 g (0.046 mol) of **3**. After stirring at 25 °C for 30 min, the mixture was diluted with water, extracted with isohexane,[22c] washed with sodium bicarbonate, and dried ($MgSO_4$). Filtration, concentration, and distillation gave 8.8 g (78%) of **4/5/6** (83:16:1).

C. To 50 mL of pyridine and 4.6 g (0.30 mol) of phosphorus oxychloride was added 6.6 g (0.025 mol) of **3** at 0 °C. The solution was stirred 3 h and then poured on ice. Extraction with isohexane[22c] and distillation gave 5.4 g (89%) of **4/5/6** (6.6:1:12.4).

Separation of Alkenes 4, 5, and 6. To a warm solution of 68.0 g of picric acid in 500 mL of 95% ethanol was added 48.8 g of a mixture of alkenes **4**, **5**, and **6**. After standing overnight, the picrate was filtered out. Two successive concentrations of the filtrate gave a second and third crop of picrates and mother liquor. The first crop of picrate (45 g) was recrystallized from ethanol to give 35 g of bright red picrate, mp 96–97 °C. Cleavage of this picrate by continuous extraction[23] with isohexane over Merck neutral alumina followed by recrystallization of the alkene from isohexane[22c] gave 13.5 g of (*E*)-2-(1-naphthyl)-1-phenylpropene (**4**): mp 36–37 °C; IR (NaCl) 915 (m), 860 (m), 800 (s), 775 (s), 750 (s), 705 (s), 695 cm^{-1} (s); ^1H NMR (CCl_4) δ 2.30 (d, J = 1 Hz, 3, CH_3), 6.52 (s, 1, vinyl H), 7.00–8.02 (m, 12, ArH); MS *m/e* (rel intensity) M^+ 244 (93), 230 (20), 229 (100), 166 (26), 165 (35), 152 (20); UV nm (log ϵ) 95% ethanol 222.5 (4.79), 245 (4.15), 282.5 (4.04). Anal. Calcd for $C_{19}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.31; H, 6.58.

The second crop of picrate (25 g) was recrystallized from ethanol to give 10.2 g of a mixture consisting of picrates from **4** and **6**. The mother liquor was evaporated to give 15.4 g of the yellow picrate of **6**, mp 80–95 °C. Attempted recrystallization resulted in dissociation. The picrate was cleaved as above and the recovered hydrocarbon was recrystallized from isohexane[22c] to give 6.0 g of 2-(1-naphthyl)-3-phenylpropene (**6**): mp 26–27 °C; IR (NaCl) 900 (m), 795 (s), 775 (s), 745 (m), 695 (s) cm^{-1}; ^1H NMR (CCl_4) δ 3.68 (s, 2, CH_2), 5.08 (d, J = 2 Hz, 1, vinyl H), 5.22 (d, J = 2 Hz, 1, vinyl H), 6.94–8.02 (m, 12, ArH); MS *m/e* (rel intensity) M^+ 244 (37), 165 (11), 154 (32), 153 (8), 152 (100), 91 (26); UV nm (log ϵ) 95% ethanol 225 (4.77), 282.5 (3.85). Anal. Calcd for $C_{19}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.06; H, 6.66.

The third crop of picrate (30.6 g) consisted of picrates of **4** and **6**. The mother liquor consisted of **5** and picric acid but no picrate could be isolated. The mixture was separated on alumina as above and recrystallized from isohexane[22c] to give 5.5 g of (*Z*)-2-(1-naphthyl)-1-phenylpropene (**5**): mp 27–28 °C; IR (NaCl) 915 (m), 860 (m), 800 (s), 775 (s), 690 cm^{-1} (s); ^1H NMR (CCl_4) δ 2.24 (d, J = 1 Hz, 3, CH_3), 6.64–7.88 (m, 15, vinyl H, ArH); MS *m/e* (rel intensity) M^+ 244 (100), 230 (19), 299 (100), 228 (26), 166 (17), 165 (27); UV nm (log ϵ) 95% ethanol 225 (4.87), 245 (4.28), 285 (3.98). Anal. Calcd for $C_{19}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.30; H, 6.94.

***threo*-2-(1-Naphthyl)-1-phenyl-1,2-propanediol (7).** To a magnetically stirred solution of 1.0 g (3.93 mmol) of OsO_4 in 25 mL of ether and 2 mL of pyridine was added 960 mg (3.93 mmol) of **4** in 5 mL of ether. After 60 h, 70 mL of ethanol and 7.0 g of Na_2SO_3 in 12 mL of H_2O were added and the mixture was heated at reflux for 3 h. The solution was cooled and filtered through Dicalite, the Dicalite was rinsed with ethanol, and the filtrate was concentrated to a small volume under reduced pressure. The residue was extracted with ether and the extract was dried ($MgSO_4$), filtered, concentrated, and then recrystallized from isohexane[22c] to give 470 mg (43%) of **7**: mp 102–104 °C; IR (CCl_4) 3570 cm^{-1} (OH) (m); ^1H NMR (80 mg/0.5 mL of $CDCl_3$) δ 1.40 (s, 3, CH_3), 3.20 (s, 1, OH), 3.22 (s, 1, ArCH), 5.46 (s, 1, OH), 6.72–8.86 (m, 12, ArH); MS *m/e* (rel intensity) M^+ 278 (4), 171 (20), 170 (100), 154 (12), 126 (12). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.66; H, 6.44.

Cyclic Boronate 8. The cyclic boronate **8** of **7** was prepared by adding 32 mg (0.328 mmol) of phenylboronic acid and 0.5 mL of $CDCl_3$ to 80 mg (0.328 mmol) of **7** in 0.5 mL of $CDCl_3$, shaking for 5 min, and filtering through glass wool. ^1H NMR ($CDCl_3$) δ 2.10 (s, 3, CH_3), 5.88 (s, 1, ArCH), 6.70–8.20 (m, 17, ArH).

***erythro*-2-(1-Naphthyl)-1-phenyl-1,2-propanediol (9).** The diol **9** was prepared as above using 865 mg (3.40 mmol) of OsO_4 and 830 mg (3.40 mmol) of **5**, giving 300 mg (32%) of **9**: mp 109–110.5 °C; IR (CCl_4) 3500 (m), 3450 cm^{-1} (OH) (m); ^1H NMR (80 mg/0.5 mL of $CDCl_3$) δ 1.66 (s, 3, CH_3), 2.28 (d, 1, OH), 2.38 (s, 1, ArC**H**), 5.34 (d, 1, OH), 7.00–8.80 (m, 12, ArH); MS *m/e* (rel intensity) M^+ 278 (2), 171 (29), 170 (100), 154 (9), 126 (12). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.11; H, 6.60.

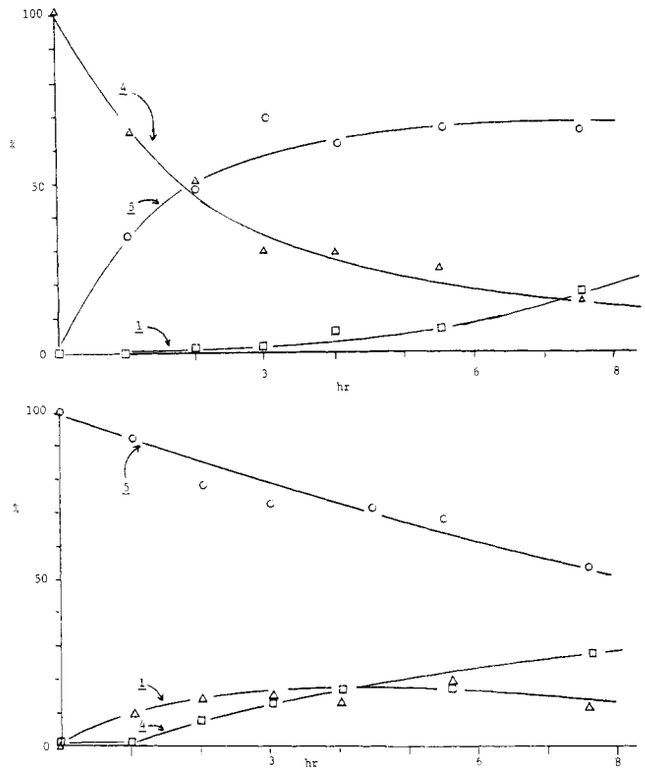


Figure 1. Photolysis of *E* and *Z* alkenes **4** and **5** (0.01 M) in benzene with I_2 (0.001 M) and saturated with O_2 reactor; (Rayonet reactor; irradiation at 3600 Å).

The cyclic boronate **10** of **9** was prepared as above; ^1H NMR ($CDCl_3$) δ 1.62 (s, 3, CH_3), 6.02 (s, 1, ArCH), 7.34–8.28 (m, 17, ArH).

5-Methylchrysene (1). To 15 L of benzene were added 12.2 g (50 mmol) of alkene mixture (**4/5/6**; 5.3:4.0:1.1) obtained by acid-catalyzed equilibration of **4**, **5**, and **6** and 0.64 g (5 mmol) of I_2. The solution was thoroughly mixed and a 3-L aliquot was transferred to a 5-L beaker. Air was bubbled through the aliquot for 30 min, the air bubbler was removed, and irradiation was begun (Hanovia, 450-W, medium-pressure, Hg lamp equipped with Corex filter). After 4 h the irradiation was stopped, the solution was removed, and the process was repeated until all 15 L were irradiated. After photolysis, the solvent was removed and the resulting oil was placed on a Soxhlet column[23] of Merck basic alumina and eluted for 24 h with isohexane.[22c] Subsequent concentration and crystallization yielded 3.6 g (29%) of 5-methylchrysene, mp 115–117 °C. A sample recrystallized from isohexane[22c] and benzene had mp 117–117.5 °C (lit.[5] mp 117 °C): ^1H NMR ($CDCl_3$) δ 3.15 (s, 3, CH_3), 7.40–7.80 (m, 8, ArH), 8.52–8.64 (m, 2, C-10 and C-11 protons), 8.82 (m, 1, C-4 proton); MS *m/e* (rel intensity) M^+ 242 (100), 241 (39), 240 (14), 239 (28), 120 (18), 119.5 (22); UV nm (log ϵ) 95% ethanol 271 (5.00), 286.5 (4.00), 300.5 (3.96), 312.5 (4.10), 326.5 (4.08).

The individual alkenes **4**, **5**, and **6** were irradiated at 3600 Å in quartz tubes in a Rayonet Reactor. Each alkene solution in benzene was 0.001 M in alkene, 0.001 M in I_2, and saturated with O_2. Samples were periodically removed and analyzed by GC.[8]

Registry No.—**1**, 3697-24-3; **2**, 1333-52-4; **3**, 65059-25-8; **4** picrate, 65059-26-9; **6** picrate, 65059-27-0; benzyl chloride, 100-44-7; picric acid, 88-89-1; phenylboronic acid, 98-80-6.

References and Notes

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(9) Amberlyst-15 resin is a sulfonic acid resin available from Rohm and Haas Company, Philadelphia, Pa. We are grateful for a research sample.
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Isomerization of 2- and 3-Carene Oxides over Solid Acids and Bases[1]

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The reaction of 3-carene oxide catalyzed by solid acids and bases gave ten compounds and several unidentified products. The main products were carbonyl compounds (IV, VI, and VII) and allylic alcohols (IX and X) with a three-membered ring except for the case of H_2SO_4/SiO_2, which gave a large amount of III, V, and VIII. The carbonyl compounds were predominantly formed over SiO_2–Al_2O_3, Al_2O_3 A and $FeSO_4$, while the allylic alcohols were preferentially formed over Al_2O_3 C and TiO_2–ZrO_2. The reactivity of 2-carene oxide over solid acids and bases was exceedingly high in comparison with that of 3-carene oxide, and eight compounds and several unidentified products were observed. All the products were the three-membered ring-opened ones. The formation of allylic alcohols with the hydroxyl group rearranged to the 3 or 8 position was also observed. A large amount of III and XIII was formed. TiO_2–ZrO_2 showed 100% selectivity for the formation of XIII at 30 °C. It is significant that the breaking of the C(3)–O bond of oxygen is much more favorable with 3-carene oxide, while the C(2)–O bond is broken with 2-carene oxide.

Introduction

Among many studies on the rearrangement of α-pinene, limonene, caryophyllene and other terpene epoxides,[2–8] there are some studies dealing with the carene oxides. In the presence of zinc bromide, 3-carene oxide rearranged mainly to the ring-contracted aldehyde and to the ketones with retention of the three-membered ring.[9–11] Joshi and co-workers reported that passing the epoxide over active alumina yielded bicyclic unsaturated alcohols together with some by-products.[11] As for 2-carene oxide, allylic alcohols with the three-membered ring intact were predominantly formed with lithium diethylamide, a strong base,[12] while the three-membered ring was

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