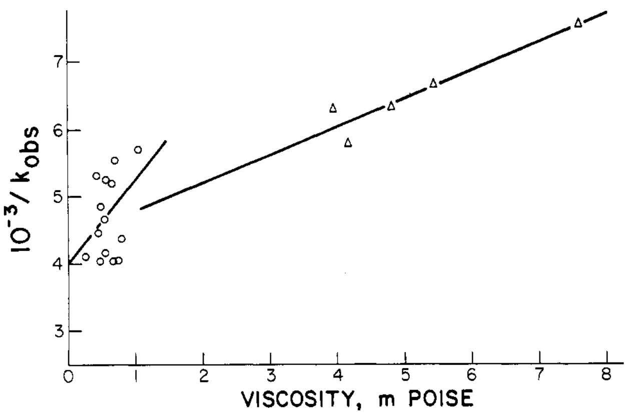

Figure 1. Plot of $10^{-3}/k_{obsd}$ against viscosity. The line is the least-squares line for the conventional solvents (△).

runs, some of which deviated by more than 100%. The activation energy from the complete set of runs was 27.99 kcal/mol and the correlation coefficient 0.867. The activation energy after dropping about half of the runs was 27.3 kcal/mol and the correlation coefficient 0.967. This activation energy is close to that reported for benzene, 24.4 kcal/mol.[9]

The 27.3 kcal/mol activation energy was used to adjust the rate constants of the remaining runs to a common temperature of 50 °C, giving a mean value of 2.16×10^{-4} s^{-1} and a standard deviation of 0.27×10^{-4}. The small variation remaining in this set of adjusted rate constants was then tested for correlations with solvent parameters.

The regression of $10^{-3}/k_{obsd}$ against the viscosity (the range of viscosity was from 0.25 to 1.02 mP) had a slope of 1.21 and a correlation coefficient of only 0.37, indicating a very small and not significant association of higher rate constants with lower viscosities. Neuman's data[2] for a very different range of viscosities (3.95–7.58 mP), for octane and four aromatic solvents, gave a slope of 0.42 and a correlation coefficient of 0.94. As shown in Figure 1, this regression line, extended toward lower viscosities, passes through the group of CO_2 points. Regression of the combined data sets gives a slope of 0.40 and $r = 0.87$. It should be noted that correlations of rates with functions of the viscosity have been reported to break down for viscosities below about 7 mP.[10]

Regression of $\log_{10} k_{obsd}$ against CO_2 π^* values (which ranged from −0.12 to −0.61)[11] gave a slope of −0.12 and a correlation coefficient of only −0.28. Neuman's data for octane and four aromatic solvents (π^* −0.08 to +0.59) also showed no significant correlation with π^*. The combined data sets had a slope of −0.18 and $r = -0.73$.

Conclusions. The correlation of the rates in supercritical CO_2 with the viscosity has to be very slight and may not be real. This means that geminate recombination of phenyldiazenyl and trityl radicals cannot be very important in CO_2. If so, k_{obsd} should be greater than the k_{obsd} values for more viscous nonpolar media, in which geminate recombination is important. The rate constants reported for some conventional solvents compare with our k_{obsd} at 50 °C as shown in Table I.

Table I

solvent	10^4K, s^{-1}	solvent	10^4K, s^{-1}
CO_2	2.17 ± 0.27	benzene[2]	1.37 ± 0.01
octane[2]	1.59 ± 0.04	benzene[9]	1.24[a]
toluene[2]	1.73 ± 0.01	cyclohexane[9]	0.96[a]

[a] At 49.9 °C.

In the limit of no geminate recombination of trityl and phenyldiazenyl radicals, k_{obsd} should be equal to k_1. The value predicted by Neuman and Lockyer from their viscosity studies[2,12] was 10.0×10^{-4} s^{-1} at 60 °C. Our k_{obsd}, adjusted to that temperature, is somewhat smaller, 7.69×10^{-4} s^{-1}.[13]

Experimental Section

Phenylazotriphenylmethane (PAT). PAT,[14] mp 110–111 °C, was stored in an evacuated desiccator and protected from light.

Kinetics. The high-pressure optical cell and the method of pressurizing it with CO_2 have been described previously.[1] A known amount of PAT was put in the cell as a solution in CH_2Cl_2 and the solvent evaporated in a stream of nitrogen. The cell was then connected to the gage block assembly, evacuated to 25 μm, and filled with CO_2. The pressure at room temperature was set at a value that would give the desired pressure when the temperature was raised. The cell was heated by a metal jacket with two 80-W cartridge heaters. The temperature was monitored by a linear temperature probe and controlled by a thermocouple. The contents of the cell were mixed by the motion of a glass bead kept in a recess out of the light path during the optical density measurements. The disappearance of PAT was followed by the decrease in optical density at 460 nm.

Products. A 10–15-mg sample of PAT was weighed a small vial and the vial placed in a 21-mL stainless steel Parr reaction vessel. This vessel was evacuated to 25 μm and CO_2 pumped in to a pressure at room temperature that would give the desired pressure at the reaction temperature. Stirring was accomplished by the movement of a glass bead or of a magnetic stirring bar. The bomb was immersed in a heated oil bath. After the reaction, the bomb was cooled to 0 °C and vented through a cold trap containing CH_2Cl_2. The bomb was then warmed to room temperature and opened, and the contents were washed out with CH_2Cl_2. The two CH_2Cl_2 solutions were analyzed separately by GLC on a 0.25-mm quartz capillary column containing a nonpolar bonded phase, DB 1710.

Acknowledgment. We thank the National Science Foundation for its support of this work under Grant CHE-8217287.

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Crystal Structure of a Highly Strained Substituted Prismane

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Prismane[1] and a few substituted prismanes have been synthesized, but detailed structural data on these highly

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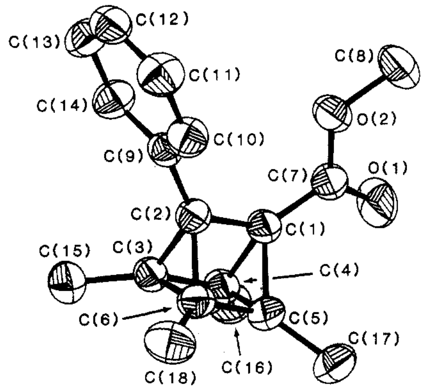

Figure 1. Perspective view of the molecular structure of compound 1.

Table I. Bond Lengths (Å) for Carbon in the Prismane

C(1)-C(2)	1.556 (3)	C(3)-C(4)	1.559 (4)
C(1)-C(4)	1.538 (4)	C(3)-C(6)	1.507 (4)
C(1)-C(5)	1.553 (3)	C(4)-C(5)	1.493 (4)
C(2)-C(3)	1.518 (4)	C(5)-C(6)	1.556 (4)
C(2)-C(6)	1.527 (3)		

Table II. Interbond Angles (deg) for Carbon in the Prismane

C(2)-C(1)-C(4)	90.8 (2)	C(1)-C(4)-C(3)	88.5 (2)
C(2)-C(1)-C(5)	90.4 (2)	C(1)-C(4)-C(5)	61.7 (2)
C(4)-C(1)-C(5)	57.7 (2)	C(3)-C(4)-C(5)	90.1 (2)
C(1)-C(2)-C(3)	89.3 (2)	C(1)-C(5)-C(4)	60.6 (2)
C(1)-C(2)-C(6)	89.6 (2)	C(1)-C(5)-C(6)	88.6 (2)
C(3)-C(2)-C(6)	59.3 (2)	C(4)-C(5)-C(6)	90.5 (2)
C(2)-C(3)-C(4)	91.4 (2)	C(2)-C(6)-C(3)	60.1 (2)
C(2)-C(3)-C(6)	60.6 (2)	C(2)-C(6)-C(5)	91.4 (2)
C(4)-C(3)-C(6)	89.8 (2)	C(3)-C(6)-C(5)	89.7 (2)

Table III. ^{13}C NMR Assignments on Compound 1[a]

carbon	chemical shift, ppm
(15, 18), (16, 17)	6.26, 6.83
(3, 6), (4, 5)	45.21, 54.83
1, 2	46.20, 48.92
8	50.47
(10, 14), (11, 13), 12	125.69, 127.65, 128.39
9	137.45
7	170.75

[a] Solvent: acetone-d_6.

strained molecules are not yet available. Hexamethylprismane, produced in low yields from photolysis of hexamethyl Dewar benzene,[2,3] was reported to be sensitive to shock and explosive at elevated temperatures.[3] These properties demonstrate the high energy of this molecule. Irradiation of several aromatic derivatives such as hexakis(trifluoromethyl)benzene,[4,5] perfluoro-1,3,5- and -1,2,4-trimethylbenzenes,[6] and perfluoropentaethylmethylbenzene[7] has led to the corresponding prismanes.

Dopper et al. prepared the chiral Dewar benzene 1,4,5,6-tetramethyl-2-phenyl-3-carbomethoxybicyclo[2.2.0]hexa-2,5-diene and reported its conversion to the corresponding prismane by irradiation at 350 nm.[8] We have carried out the synthesis of this prismane (compound 1) to characterize further its structure by X-ray diffraction methods and ^{13}C NMR. To the best of our knowledge,[9] this is the first reported X-ray crystal structure determination of a triprismatic molecule.

The molecular geometry of the prismane is shown in Figure 1, and some important bond distances and angles are presented in Tables I and II. The distances and angles within the carboxylic ester and phenyl portions of the molecule are normal.[10,11] The bond length from the prismane carbon C(1) to the carbonyl carbon C(7) is 1.451 (4) Å compared with 1.495 (19) Å for the R′COOR type of carboxylic ester.[10] The three bonds connecting the two cyclopropane portions of the prismane are equal within their esd's, with C(1)–C(2) = 1.556 (3) Å, C(3)–C(4) = 1.559 (4) Å, and C(5)–C(6) = 1.556 (3) Å. These values are comparable to those of previously reported cyclobutane bonds.[12] Crystallographic studies and molecular orbital calculations for cyclopropane rings with π-acceptor substituents indicate that distal ring bonds are shortened and vicinal bonds lengthened relative to cyclopropane itself.[13] These previous results are useful in understanding the cyclopropane portions of prismane 1. The cyclopropane C–C bonds vicinal to the phenyl ring are C(2)–C(3) = 1.518 (4) Å and C(2)–C(6) = 1.527 (3) Å while the distal bond is shorter, although not significantly, with C(3)–C(6) = 1.507 (4) Å. This effect is more pronounced in the cyclopropane portion having the carboxylic ester substituent, presumably because the carboxylic ester is a better π-acceptor than the phenyl ring. The C–C bonds vicinal to the ester functionality are C(1)–C(4) = 1.538 (4) Å and C(1)–C(5) = 1.553 (3) Å with the distal bond, C(4)–C(5) = 1.493 (4) Å, statistically shorter.

A single-crystal X-ray diffraction study of compound 1, $C_{18}H_{20}O_2$, shows that 1 crystallizes in the centrosymmetric space group $P\bar{1}$ with a = 10.525 (2) Å, b = 10.303 (2) Å, c = 7.364 (1) Å, α = 77.44 (1)°, β = 80.90 (1)°, γ = 81.66 (1)°, V = 764.5 (2) Å^3, and ρ = 1.148 g cm^{-1} for M_r 268.36 and Z = 2. Diffraction data was collected on a Syntex $P2_1$ single-crystal diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by using conventional direct methods, Fourier syntheses, and full-matrix least-squares refinements and was refined to a final $R_F = 0.043$ ($I \geq 3\sigma$) for all 1458 independent reflections with $3° \leq 2\theta \leq 45°$.[14] The crystal appeared to decompose slowly due to the X-ray beam during data collection.

With the numbering system for the carbon atoms shown in Figure 1, the ^{13}C NMR assignments are shown in Table III.

The assignments of the prismane carbons C(1)–C(6) are of interest and are made by comparing the substituent carbons with standard data. The ester carbon assignments C(7) and C(8) compare favorably with those of carbomethoxycyclobutane (175.7 and 51.40 ppm).[15] Benzene carbon atoms absorb at 128.5 ppm;[16] therefore, C(10)–C(14)

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are assigned to the signals at 125.69, 127.65, and 128.39 ppm, while C(9), the carbon atom attached to a prismane carbon, is assigned to the signal at 137.45 ppm. This is consistent with the carbon attached to the methyl group in toluene (137.4 ppm).[16] The methyl carbons, which are primary and show relatively strong signals, appear in the 0–35 ppm region for methyl carbons of alkanes.[16,17]

Among the six prismane carbons, there are four chemically different carbon atoms, and four signals are observed. Prismane itself exhibits a signal at 30.6 ppm.[1] However, substituent effects shift the signals downfield. The signals at 45.21 and 54.83 ppm are approximately equal and about twice the relative intensity of those at 46.20 and 48.92 ppm. Therefore, the former signals are assigned to the equivalent C(3),C(6) and C(4),C(5) sets, and the latter are assigned to C(1) and C(2).

Acknowledgment. We gratefully acknowlede the U.S. Army Armament Research and Development Command, Dover, NJ, for support of this work.

Supplementary Material Available: Details of data collection and structure refinement, atomic positional parameters, thermal parameters, and complete tables of bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

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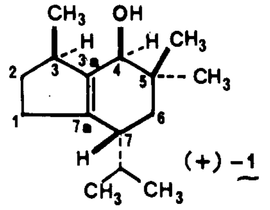
Communications

Expeditious, Stereocontrolled Syntheses of Racemic and Natural Brasilenol through Intramolecular Asymmetry Transfer. Absolute Stereochemistry of Brasilenol

Summary: Brasilenol, a marine metabolite, has been efficiently synthesized in both racemic and natural forms through the use of a highly selective palladium-catalyzed double bond migration.

Sir: (+)-Brasilenol (**1**), a metabolite from the sea hare *Aplysia brasiliana* and the red alga *Laurencia obtusa*, was first isolated in 1978 by Stallard, Fenical, and Kittredge.[1]

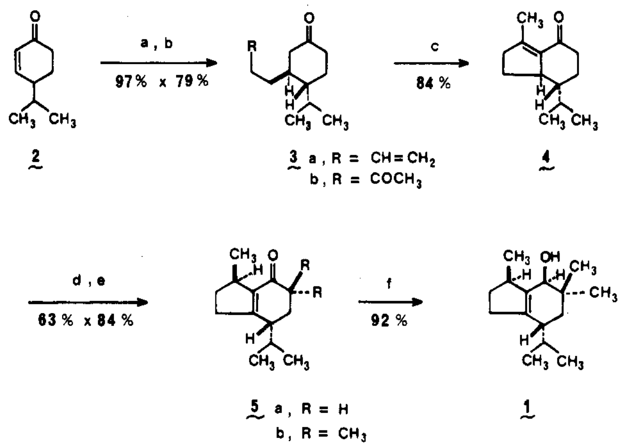


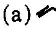
(+) –1

(+) – **Brasilenol**

The novel nonisoprenoid structure and relative stereochemistry that were formulated for this possible feeding deterrent[2] have recently been confirmed by total synthesis.[3] In this paper we report a much more effective approach to racemic brasilenol (7 steps, 31% overall yield vs. 13 steps, 5% overall yield) and the first synthesis of natural brasilenol through an unusual intramolecular transfer of asymmetry. The enantioselective synthesis serves to define for the first time the absolute stereochemistry of (+)-brasilenol and, hence, also that of (+)-4-epibrasilenol and brasilenol acetate (from *Aplysia brasiliana*).[4]

Scheme I[a]



[a] (a)  MgBr, CuI, THF; (b) $PdCl_2$, CuCl, O_2, DMF-H_2O; (c) *t*-BuOK, *t*-BuOH; (d) 10% Pd-C, H_2, C_6H_6; (e) $LiN(i\text{-}C_3H_7)_2$, THF, CH_3I (2×); (f) $LiB(C_2H_5)_3H$, THF.

Commercially available racemic cryptone (**2**)[5] underwent smooth, copper-mediated conjugate addition of 3-butenylmagnesium bromide[6] to provide stereoselectively (≥95% trans[7]) in 97% yield ketone **3a**[8] (Scheme I).

---

(1) (a) Stallard, M. O.; Fenical, W.; Kittredge, J. S. *Tetrahedron* **1978**, *34*, 2077–2081. (b) See also: Fenical, W.; Sleeper, H. L.; Paul, V. J.; Stallard, M. O.; Sun, H. H. *Pure Appl. Chem.* **1979**, *51*, 1865–1874. For an excellent review on the metabolites of marine algae and herbivorous marine molluscs, see: Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251–280.

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(3) Greene, A. E.; Coelho, F.; Barreiro, E. J.; Costa, P. R. R. *J. Org. Chem.* **1986**, *51*, 4250–4253.

(4) (+)-Brasilenol, (+)-4-epibrasilenol, and brasilenol acetate (from *Aplysia brasiliana*) have been shown to belong to the same enantiomeric series.

(5) Racemic cryptone can now be obtained from the Aldrich Chemical Co. Prior to this availability, it was discovered that **2** (essentially racemic) could be conveniently obtained in 85% yield from (+)-nopinone by treatment with 2.0 equiv of aluminum chloride in methylene chloride for 70 min at 0 °C (unpublished results). Cf.: Wallach, O. *Ann.* **1907**, *356*, 227–249; **1908**, *359*, 265–289.

(6) See: Paquette, L. A.; Galemmo, R. A., Jr.; Caille, J.-C.; Valpey, R. S. *J. Org. Chem.* **1986**, *51*, 686–695 and references cited therein.

(7) The stereochemical result of this type of addition is well precedented. See: Posner, G. *Org. React.* (*N. Y.*) **1972**, *19*, 1–113. Piers, E.; Gavai, A. V. *Tetrahedron Lett.* **1986**, *27*, 313–316. Predictably, the conjugate addition reaction of 3-butenylmagnesium bromide with α′,α′-dimethylcryptone under similar conditions afforded a mixture of cis and trans adducts.

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