freeze-dried, and the residue was purified as described for the reaction of uridine with DISN.

Reaction of Adenosine with DISN. Adenosine (0.053 g, 0.20 mmol) and DISN (0.212 g, 2.0 mmol) were dissolved in 10 mL of 0.2 M imidazole·HCl buffer (pH 7.0), and the solution was stirred at 2 °C for 3 days. The reaction mixture was filtered and the filtrate was freeze-dried. The residue was extracted with methanol and the methanol-soluble fraction was treated with Norit 211 for 1 h at room temperature. The methanol was concentrated to give a powder which was dissolved in 0.6 M boric acid and was purified by preparative TLC on silica gel by development with 1-propanol:0.3 M boric acid (9:1). A mixture of adenosine 3′-carbamate (**16**) and adenosine 2′-carbamate (**15**) was eluted in a band of R_f 0.5. The mixture was crystallized from methanol–ethanol, and the product contained a 4.5:1 ratio of **16**(41%):**15**(9%) as shown by HPLC. Further crystallization yielded a pure sample of **16**: ^{1}H NMR ($(CD_3)_2SO$) δ 3.62 (2 H, m, H-5′), 4.11 (1 H, q, $J_{4',5'}$ = 2.4 Hz, H-4′), 4.81 (1 H, dd, $J_{2',3'}$ = 5.4 Hz, H-2′), 5.10 (1 H, dd, $J_{3',4'}$ = 2.2 Hz, H-3′), 5.91 (1 H, d, $J_{1',2'}$ = 7.1 Hz, H-1′), 6.72 (2 H, br s, $OCONH_2$), 7.43 (2 H, br s, NH_2), 8.19 (1 H, s, H-8), 8.46 (1 H, s, H-8); ^{13}C NMR ($(CD_3)_2SO$) δ 59.65 (C-5′), 72.03 (C-2′), 72.83 (C-3′), 84.03 (C-4′), 87.53 (C-1′), 119.33 (C-5), 139.63 (C-8), 149.12 (C-4), 152.37 (C-2), 155.44 (carbamate), 155.96 (C-6); IR (KBr) 3360, 1720, 1645, 1600, 1478, 1420, 1400, 1335, 1305, 1250, 1205, 1125, 1084 cm^{-1}.

The NMR spectral analysis of adenosine 2′-carbamate (**15**) was performed by comparison of the NMR spectra of the mixture of **15** and **16** with that of the purified sample of **16**. The derived spectra of **15** are as follows: ^{1}H NMR ($(CD_3)_2SO$) δ 3.62 (2 H, m, H-5), 4.41 (1 H, q, $J_{4',5'}$ = 2.4 Hz, H-4′), 4.42 (1 H, dd, $J_{3',4'}$ = 3.2 Hz, H-3′), 5.51 (1 H, dd, $J_{2',3'}$ = 4.9 Hz, H-2′), 6.11 (1 H, d, $J_{1',2'}$ = 6.7 Hz, H-1′), 6.72 (2 H, br s, $OCONH_2$), 7.43 (2 H, br s, NH_2), 8.19 (1 H, s, H-2), 8.46 (1 H, s, H-8); ^{13}C NMR ($(CD_3)_2SO$) δ 61.50 (C-5′), 69.08 (C-2′), 74.62 (C-3′), 85.30 (C-4′), 86.40 (C-1′), 119.33 (C-5), 139.63 (C-8), 149.12 (C-4), 159.39 (C-2), 156.10 (C-6), 156.22 (carbamate carbon).

Reaction of Adenosine with BrCN. Adenosine (1.50 g, 5.61 mmol), BrCN (2.38 g, 22.4 mmol), and triethylamine (6.73 mL, 48.4 mmol) were dissolved in 100 mL of distilled water (initial pH 11.0), and the mixture was stirred at 2 °C for 3 h. The reaction mixture was freeze-dried and the residue was extracted with chloroform. The chloroform-insoluble fraction was extracted with methanol and the extract was concentrated to dryness. The residue was dissolved in 0.6 M boric acid and purified by preparative TLC as outlined for the reaction of adenosine with DISN. A crystalline mixture of **16** (45%) and **15** (19%) was obtained in a 2.3:1 ratio, respectively.

Reaction of Thymidine with DISN. Thymidine (0.97 g, 4.0 mmol) and DISN (2.12 g, 20.0 mmol) were dissolved in 50 mL of 0.2 M imidazole·HCl buffer (pH 7) and the mixture was stirred at 2 °C for 3 days. The reaction mixture was filtered, and the filtrate was freeze-dried and extracted with methanol. The methanol-soluble fraction was treated with Norit 211 at 0 °C for 30 min and filtered and the filtrate concentrated in vacuo to a gummy solid. Attempted purification by preparative TLC resulted in the recovery of thymidine. HPLC analysis before workup indicated an adduct of thymidine formed which was hydrolyzed to thymidine during the concentration of the methanol extract and preparative HPLC.

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Registry No. **2**, 28321-79-1; **4**, 58-96-8; **7**, 87186-13-8; **8**, 3736-77-4; **9**, 3083-77-0; **10**, 6195-72-8; **11**, 89998-91-4; **12**, 89998-90-3; **13**, 58-61-7; **15**, 89998-93-6; **16**, 89998-92-5; **17**, 50-89-5; uridine 5′-phosphate, 58-97-9; BrCN, 506-68-3.

Cyclizations of ω-Allenyl Radicals[1a]

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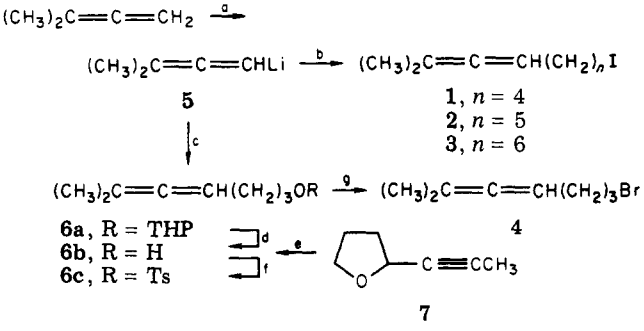
Allenyl halides of structure $(CH_3)_2C{=}C{=}CH(CH_2)_nX$ with n = 3–6 have been prepared and reacted with n-Bu_3SnH to generate the corresponding radicals for examination of the cyclization reactions of these reactive intermediates. The observed hydrocarbon products indicate that cyclization occurs for the n = 3, 4, and 5 radicals but not for the n = 6 species. The n = 3 radical isomerizes very efficiently by intramolecular addition to the sp carbon of the allene group. The n = 5 intermediate reacts relatively slowly by attack at the near sp^2 carbon. Both cyclization modes are observed for the n = 4 species. The details of these radical cyclizations are discussed.

The cyclizations of olefinic free radicals have been the subject of intense study over the past two decades, during which time a reasonable understanding of the scope of these reactions has gradually developed.[2] The analogous reactions of acetylenic radicals have also received some attention.[2,3] However, practically nothing is known concerning the intramolecular additions of free radicals to the allene function.[4,5] The unique bonding situation char-

Scheme I[a]



[a] a, RLi; b, $I(CH_2)_nI$; c, $Br(CH_2)_3OTHP$; d, TsOH, MeOH; e, $(CH_3)_2CuLi$; f, TsCl; g, $MgBr_2$.

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Table I. Reduction of Allenyl Halides by Bu_3SnH

react-ant	solvent	yield	product ratios 8	9	10	10	other
4	C_6H_6	90%	45	51			4[a]
	neat		39	42	17		2[a]
1	C_6H_6	80%	4	27	20	49	
	neat				100		
2	C_6H_6	91%			60	23	17[b]
	neat				100		
3	C_6H_6	75%			90		7, 3[c]

[a] Unknown product. [b] 2-Methyl-2,4-nonadienes. [c] 2-Methyl-2,4-decadienes and 2-methyl-1,3-decadienes, respectively.

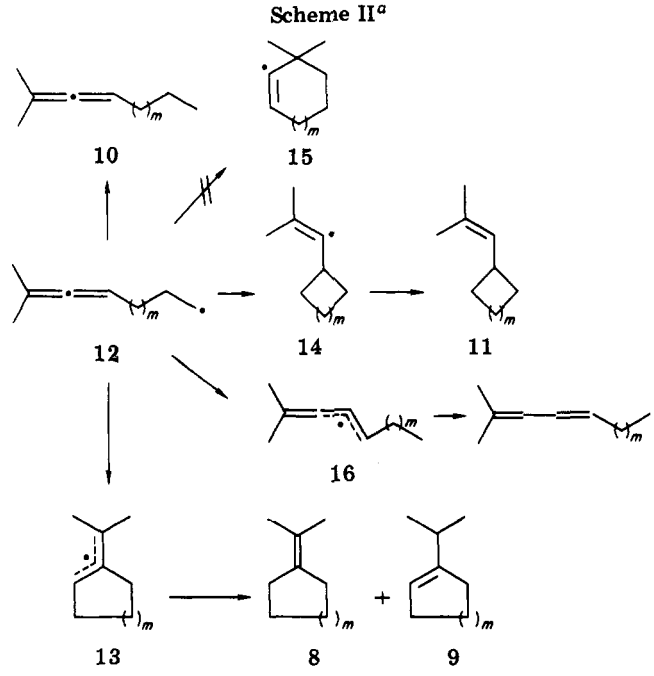
acteristic of allenes suggests that such reactions should provide an interesting comparison with those of olefinic and acetylenic analogues. Furthermore, the anticipated cyclizations are of substantial synthetic potential for the formation of usefully functionalized carbocycles. In the present contribution we describe studies on the chemistry of various allene-substituted free radicals.

Results

The synthesis of the starting materials utilized in this work is indicated in Scheme I. With a view toward the adaptation of the widely utilized tin hydride methodology for the generation of free radicals,[6] halo allenes with varying numbers of methylene groups between the two functional groups were prepared. Practical synthetic considerations led to the use of the series with geminal methyl groups at one end of the allene group in these initial studies. The compounds **1–3** were conveniently obtained by the alkylation of the allenyllithium reagent **5** derived from 3-methyl-1,2-propadiene with the appropriate diiodoalkane according to the procedure of Linstrumelle.[7] (An improved procedure for the preparation of 3-methyl-1,2-propadiene is given in the Experimental Section.) The modest yields in these reactions and the necessity for chromatographic separation of the products from unreacted halides were more than compensated for by the directness of this route. Several attempts to use 1,3-diiodopropane in a similar approach to the next lower homologue unaccountably failed. Consequently, two alternate syntheses of **4** were developed. In the first of these, allenyllithium **5** was alkylated with the tetrahydropyranyl ether of 3-bromo-1-propanol in THF containing HMPA to give **6a**. Removal of the protecting group from **6a** gave alcohol **6b**. Alcohol **6b** was also obtained by the reaction of lithium dimethylcuprate with tetrahydrofuran **7**,[8] which is readily prepared from 2-chlorotetrahydrofuran and the lithium derivative of propyne. Difficulty in the conversion of alcohol **6b** to the corresponding iodide was circumvented by preparing bromide **4** by treating tosylate **6c** with $MgBr_2$.[9]

Each of the halides **1–4** were reacted with Bu_3SnH as dilute solutions in refluxing benzene. In addition, **1**, **2**, and **4** were treated with neat tin hydride. The reaction mixtures were analyzed by GC and the products were isolated by concentration of the reaction mixtures and subsequent preparative GC separation. The identities of the products were demonstrated by comparison with authentic samples unless otherwise indicated. The results are summarized in Table I.

Scheme II[a]



[a] a, $m = 1$; b, $m = 2$; c, $m = 3$; d, $m = 4$; e, $m = 0$.

Discussion

This study demonstrates that, as expected, the allenyl radicals **12** (Scheme II) undergo cyclizations related to those of their olefinic counterparts. The facility and regiochemistry of these intramolecular radical additions depend substantially on the length of the carbon chain separating reactive functions. The presence of two double bonds joined cumulatively obviously complicates the situation relative to the simple olefinic analogues, but cyclizations of allenyl radicals **12** also appear to be kinetically controlled.[2] In particular, the much greater thermodynamic stability of the allylic radicals **13** relative to the vinyl radicals **14** does not dominate the cyclization mode to the extent that might have been expected. However, this is not totally unanticipated since the *inter*molecular addition of radicals to allenes is well-known to show a similar disregard for intermediate radical stability in many instances.[10] On the other hand, the size of the ring to be generated is clearly an important consideration in determining the fate of allenyl radicals **12**. This was noted previously with the homoallenyl radical **12e** which chooses the three-membered ring over the four-membered ring mode of cyclization in accordance with normal chemical behavior in ring formation.[4,11]

Allenyl radical **12a** ($m = 1$) enjoys the favorable situation of being able to cyclize to allylic radical **13a** with formation of a preferred five-membered ring. This accounts for the highly selective generation of products **8a** and **9a** from this intermediate. The relatively inefficient trapping of the acyclic radical **12a** even in neat Bu_3SnH attests to the high

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rate of the **12a** → **13a** transformation. Under these conditions the product ratio indicates a relative rate ratio of about 4.8 for cyclization vs. hydrogen abstraction by **12a**. By way of comparison, a comparable experiment with 5-hexenyl radical gives a 0.053 ratio of methylcyclopentane to 1-hexene. If the reasonable assumption of equal rates for hydrogen abstraction by **12a** and the 5-hexenyl radical is valid,[12] then cyclization of allenyl radical **12a** is about 90 times faster than that of its simple olefinic counterpart. While this is a significant factor, it probably does not fully reflect the much larger thermochemical advantage of the allene cyclization which benefits both from the "strain"[13] associated with the allene function in **12a** and allylic stabilization in **13a**. This suggests an early transition state that does not profit excessively from allylic radical stabilization. Conformational features are probably important in determining the mode of cyclization for **12a**, since molecular models indicate that the radical center can approach within ca. 2Å of the sp-hybridized carbon without bond angle distortion, whereas either of the sp^2 carbons are at ca. 2.5 Å in the closest arrangement for intramolecular attack. The cyclization of **12a** must be influenced by these restrictions imposed by the short carbon chain which favor the formation of **13a** over alternatives **14a** and **15a**.

The situation is not as unambiguous for allenyl radical **12b** ($m = 2$) which reacts by several competitive pathways. The observation of allene **10b** as a product under dilute solution conditions indicates that **12b** cyclizes more slowly than its lower homologue **12a** and the 5-hexenyl radical. The fact that only allene **10b** is produced from **12b** in neat Bu_3SnH means that the cyclization of radical **12b** is at least several hundred times slower than that of **12a**. In this case the cyclization of **12b** to vinyl radical **14b** is competitive with isomerization to allylic radical **13b**. The rate of five-membered ring formation is about 1.6 times that of the six-membered ring process. Thus, the usual preference for radical cyclizations to give five-membered rings is an important consideration with this allenic system.[2] However, the margin is appreciably smaller than the 50:1 ratio for cyclopentane vs. cyclohexane cyclization found for the 5-hexenyl radical.[2] Much of this difference may be attributable to radical stability considerations. Molecular models of **12b** do not indicate undue restrictions to the close approach of the radical center to any of the three carbons of the allene function. Thus, considerations akin to those proposed to account for the regioselectivity of the 5-hexenyl radical are undoubtedly applicable to **12b** as well.[2]

As expected, allenyl radical **12c** ($m = 3$) is trapped by Bu_3SnH prior to isomerization even more efficiently than its lower homologue. The cyclization which does occur proceeds with regioselective six-membered ring formation to give vinyl radical **14c**. Interestingly, this selectivity appears to be higher than the 6:1 ratio observed for the 6-heptenyl radical.[2a] If a constant rate for hydrogen abstraction by the acyclic radicals is assumed, the **12c** → **14c** isomerization is only about 0.16 times as fast as the **12b** → **14b** conversion.

A different type of reaction appears to be important for **12c**, namely a 1,5-hydrogen transfer resulting in the stabilized radical **16c**. This is deduced from the formation of 2-methyl-2,4-nonadiene. An acid-catalyzed route to this product is ruled out by the absence of 1-methyl-1,3-nonadiene, which is the major product expected from acid isomerization of allene **10c**. (A study of the acid-catalyzed isomerization of lower homologue **10b** is described in the Experimental Section.) A similar 1,5-hydrogen transfer has been documented for the 6-heptenyl radical.[14]

Finally, radical **12d** ($m = 4$) does not give significant amounts of cyclic products under the dilute solution conditions utilized. In this case cyclization is not fast enough to compete with the bimolecular reaction of **12d** with Bu_3SnH. The conjugated dienes observed as minor products from allenyl iodide **3** are probably derived from acid-catalyzed isomerization of the allene function before, during, or after the Bu_3SnH reaction. This follows from the presence of both 1,3- and 2,4-dienes as expected for an acid-catalyzed process.

In summary, allenyl radicals **12** cyclize to isomeric radicals **13** and/or **14** with efficiencies which decrease from 100% to 0% with increasing chain length. The regioselectivities for **13** vs. **14** are also controlled by chain length which determines both the mode and the degree of selectivity. Finally, cyclization to radical **15** by attack at the remote sp^2 carbon is not a competitive process for any of the allenyl radicals studied.

Experimental Section

General Methods. Infrared spectra (IR) were recorded on thin films by using Perkin-Elmer Model 397 and 467 spectrometers. Nuclear magnetic resonance (NMR) spectra were obtained as CCl_4 solutions on Hitachi-Perkin Elmer R24A (60 MHz), Varian EM-390 (90 MHz), and HR-220 (220 MHz) and Nicolet NT-360 (360 MHz) instruments. Gas chromatography (GC) separations were performed on Varian Aerograph 600D (analytical) and A700 (preparative) instruments. Thin-layer chromatography (TLC) utilized silica gel 1B2F Baker-flex plates and column chromatography was carried out over Merck Kieselgel 60 (ASTM 70–230 mesh). Elemental analyses were performed by the Central Analytical Service of the CNRS and Midwest Microlabs, Inc.

Solvents were redistilled just prior to utilization from lithium aluminum hybride for ether and THF and from sodium for benzene. Sodium sulfate was routinely employed as a drying agent.

1-Bromo-3-methyl-1,2-butadiene. The method of Landor et al.[15] was used. After the indicated period of stirring, the product was decanted and dried over K_2CO_3. The crude product obtained in this manner in 92% yield was utilized directly in the preparation of 3-methyl-1,2-butadiene.

3-Methyl-1,2-butadiene. The Zn–Cu couple prepared by the literature method[16] was washed with 1-propanol. Into a 500-mL, 3-necked flask fitted with a mechanical stirrer, a thermometer, and efficient condenser was placed 58 g of Zn–Cu couple, 49 g (0.3 mol) of 1-bromo-3-methyl-1,2-butadiene, and 150 mL of 1-propanol. The reaction mixture was gently heated to 65 °C at which point an exothermic reaction occurred, causing the temperature to rise to ca. 80 °C for a period of 15 min. After the reaction mixture had cooled to room temperature, the condenser was replaced with a Vigreux column and a fraction boiling at 36–65 °C was removed by distillation. The products from five such experiments were combined and redistilled through an efficient column to give 73 g (72%) of the allene, bp 39–40 °C.[17]

1-Iodo-9-methyl-7,8-decadiene (3). Into a dry 3-necked flask equipped with a dropping funnel, an N_2 inlet, and a rubber septum was placed 29 mL (38 mmol) of 1.3 M methyllithium in ether and several drops of diisopropylamine. A solution of 9.6 g (140 mmol) of 3-methyl-1,2-butadiene in 10 mL of ether was added dropwise at room temperature and the reaction was allowed to proceed until

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there was no further gas evolution (ca. 2 h). At this point HMPA was added carefully by syringe until the solution just became cloudy (ca. 1 equiv per equiv of methyllithium). This solution was transferred to a dropping funnel under N_2 and added over 0.5 h to a magnetically stirred solution of 14 g (41 mmol) of 1,6-diiodohexane in ether at −10 °C. A precipitate began to form almost immediately. After 1 h the reaction was complete as indicated by TLC analysis. Hydrolysis was effected by the addition of 50 mL of water. The reaction mixture was extracted with ether and the extract was dried and concentrated to give an oil. This was chromatographed over silica gel using pentane as eluant to give 4.8 g (41%) of **3**: bp ca. 88 °C (0.25 torr); NMR δ 1.1–2.2 (m, 10), 1.64 (d, 6), 3.12 (t, 2) and 4.80 ppm (m, 1); IR 1965 cm^{-1}. This material decomposes upon standing. Anal. Calcd for $C_{11}H_{19}I$: C, 47.48; H, 6.71; I, 45.68. Found: C, 47.5; H, 6.8; I, 45.0.

1-Iodo-7-methyl-5,6-octadiene (1). Into a dry 100-mL flask equipped with a dropping funnel and a magnetic stirrer was placed a solution of 5.48 g (0.08 mol) of 3-methyl-1,2-butadiene in 40 mL of dry THF under N_2. The mixture was cooled to −78 °C and 1 equiv of a solution of *n*-butyllithium in pentane was added dropwise. After stirring for 1 h, 25.5 g (0.08 mol) of 1,4-diiodobutane was added rapidly. A precipitate began to form almost immediately. The reaction mixture was allowed to warm to room temperature. After 4 h, water was added and the resulting mixture was extracted with ether. The extract was dried and concentrated and the resulting oil was chromatographed on silica gel using hexane as eluant to separate the product from unreacted diiodide. Distillation gave 12.5 g (62%) of pure **1**: bp 44–46 °C (0.01 torr); NMR δ 1.2–2.2 (m, 6), 1.68 (d, 6), 3.15 (t, 2), and 4.87 ppm (m, 1); IR 1975 cm^{-1}. Anal. Calcd for $C_9H_{15}I$: C, 43.20; H, 6.05; I, 50.76. Found: C, 43.4; H, 5.8; I, 50.5.

1-Iodo-8-methyl-6,7-nonadiene (2). In a similar experiment the organolithium reagent was prepared from the reaction of 2.7 g (0.04 mol) of 3-methyl-1,2-butadiene in 40 mL of THF with 20 mL (0.04 mol) of 2.1 M *n*-butyllithium in pentane and reacted with 13.0 g (0.04 mol) of 1,5-diiodopentane. Chromatography gave ca. 40% of pure **2**: NMR δ 1.2–2.2 (m, 14), 3.15 (t, 2), 4.85 ppm (m, 1); IR 1955 cm^{-1}. Anal. Calcd for $C_{10}H_{17}I$: C, 45.45; H, 6.44; I, 48.10. Found: C, 45.5; H, 6.5; I, 48.2.

2-(1-Propynyl)tetrahydrofuran (7). Into a solution of 0.15 mol of ethylmagnesium bromide in ether in a 3-necked flask equipped with an efficient stirrer, a Dry-Ice condenser, and an inlet tube was passed an excess of propyne. After 1 h a second phase separated; stirring was continued until the lower phase no longer increased in volume (ca. 3 h). The mixture was cooled to −15 °C and 15 g (0.14 mol) of 2-chlorotetrahydrofuran[18] in 30 mL of ether was added over 20 min, causing the formation of a precipitate. After 1 h at −15 °C the mixture was allowed to warm to room temperature and hydrolyzed by the addition of an ammonium chloride solution. The ether layer was removed, dried, and concentrated to give an oil which was distilled to give 13.5 g (87%) of **7**: bp ca. 65 °C (25 torr); NMR δ 1.7–2.1 (m, 7), 3.7 (m, 2), and 4.4 ppm (m, 1); IR 2230, 1050 cm^{-1}. Anal. Calcd for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.4; H, 9.1.

6-Methyl-4,5-heptadien-1-yl Tetrahydropyranyl Ether (6a). A solution of dimethylallenyllithium was prepared as described above from 31.3 g (0.46 mol) of 3-methyl-1,2-butadiene and 100 mL (0.13 mol) of 1.3 M methyllithium. Gas evolution ceased after 11 h and HMPA was then added until the solution just became cloudy (ca. 10 mL). 3-Bromopropyl THP ether[19] (14 g, 0.062 mol) in 20 mL of ether was added over a 10-min period. After several hours most of the starting material had reacted as indicated by GC and hydrolysis was effected with a saturated solution of NH_4Cl. The mixture was thoroughly extracted with ether and the extract was washed, dried, and concentrated. GC of the crude product indicated the presence of a low-boiling material and three longer retention time products in the proportions 6:6:88, the first of which was identical with starting material. Distillation gave 2 g of a fraction of bp ca. 28 °C (0.8 torr) and 9.0 g of a fraction of bp ca. 85 °C (0.8 torr). The first fraction was identified as allyl tetrahydropyranyl ether by comparison with an authentic sample prepared from allyl alcohol. The second fraction was chromatographed on silica gel using hexane–ethyl acetate (10:1) as eluent to give 7.7 g (59%) of **6a**: NMR δ 1.3–2.3 (m, 10), 1.65 (d, 6) 3.5 (m, 4), 4.45 (b, s, 1), and 4.85 ppm (m, 1); IR 1965, 1035 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.28; H, 10.47; O, 15.24. Found: C, 74.4; H, 10.2; O, 15.5.

6-Methyl-4,5-heptadien-1-ol (6b). A. A solution of 2.0 g of **6a** and several milligrams of *p*-toluenesulfonic acid in 30 mL of methanol was allowed to react at room temperature for 5 h. The mixture was concentrated under vacuum in the cold and the residue was taken up in ether, washed with $NaHCO_3$ solution and water, and dried. Removal of the solvent gave 1.2 g of crude **6b**.

B. Into a 3-necked flask fitted with a dropping funnel, a condenser, a septum, and a magnetic stirrer was placed 11.4 g (60 mmol) of pulverized CuI. The flask was flamed while stirring under a stream of N_2. Dry ether (60 mL) was added and the mixture was cooled to −10 °C before the dropwise addition of a solution of methyllithium in ether (ca. 120 mmol) until a clear pink solution was obtained. Over a 2-min period, 2.2 g (2.1 mmol) of **7** was added by syringe. The reaction mixture was allowed to warm to room temperature with the formation of a yellow precipitate. The reaction was complete after 4 h as indicated by GC. The mixture was hydrolyzed by the addition of saturated NH_4Cl solution and extracted with ether. The extract was dried and concentrated to give a 2.5 g (94%) of essentially pure product: bp ca. 69 °C (3 torr); NMR δ 1.2–2.3 (m, 4), 1.66 (d, 6), 2.50 (s, 1), 3.65 (t, 2, J = 6 Hz) and 4.88 ppm (m, 1); IR 3320, 1965 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.0; H, 11.1.

Purification of CuI. The CuI was purified by adding 13.1 g of CuI to a solution of 130 g of KI in 100 mL of distilled water and stirring until completely dissolved. Activated charcoal (1 g) was added and the mixture was stirred for 10 min before filtering through Celite. CuI was precipitated by the addition of distilled water, and the product was collected by filtration and washed four times with 80-mL portions of acetone and four times with 80-mL portions of ether. The CuI thus obtained was dried under vacuum.

6-Methyl-4,5-heptadien-1-yl *p*-Toluenesulfonate (6c). To a solution of 2.73 g (21.6 mmol) of **6b** in 50 mL of pyridine at 0 °C was added 8.25 g (43.3 mmol) of *p*-toluenesulfonyl chloride. After 20 h the mixture was poured into an ice–water mixture and extracted with ether. The extract was washed thoroughly with dilute HCl and dried, first over K_2CO_3 and then with Na_2SO_4. Removal of the solvent gave 5.77 g (95%) of crude **6c**: NMR δ 1.6–2.3 (m, 4), 1.62 (d, 6), 2.43 (s, 3), 3.97 (t, 2), 4.81 (m, 1) and 7.5 ppm (m, 4); IR 1960, 1595, 1490, 1380, and 1170 cm^{-1}. This material was used without purification in the preparation of **4**.

1-Bromo-6-methyl-4,5-heptadiene (4). In a 2-L flask equipped with a mechanical stirrer and a reflux condenser was placed 4.9 g of powdered Mg and 800 mL of dry ether. The addition of 36 g of $HgBr_2$ produced an exothermic reaction and reflux was continued for 2 h. This mixture was filtered into a second flask equipped with a mechanical stirrer and 5.75 g of **6c** in 50 mL of ether was added. This caused the rapid formation of a white precipitate. After 6 h TLC indicated the disappearance of the tosylate. The mixture was hydrolyzed by the addition of 100 mL of water. The organic layer was separated, washed twice with a K_2CO_3 solution, and dried first over K_2CO_3 and then over Na_2SO_4. Removal of the solvent gave an oil which was purified by chromatography on silica gel using hexane–ethyl acetate (10:1) to give 2.92 g (75%) of **4** which was 97% pure by GC: bp ca. 56 °C (1 torr); NMR δ 1.66 (d, 6) 2.0 (m, 4), 3.34 (t, 2), and 4.84 ppm (m, 1); IR 1965 cm^{-1}. This material decomposed upon standing. Anal. Calcd for $C_8H_{13}Br$: C, 50.79; H, 6.88; Br 42.33. Found: C, 50.3; H, 6.7; Br, 41.9.

1-Isopropylcyclohexene (9b) and Isopropylidenecyclohexane (8b).[20] A solution of isopropylmagnesium bromide prepared in the usual fashion from 0.1 mol of isopropyl bromide was reacted with 0.05 mol of cyclohexanone. Workup in the usual manner gave 5.2 g of a mixture of cyclohexanol and 1-isopropylcyclohexanol. This mixture was heated to reflux in the presence of a small amount of *p*-toluenesulfonic acid until the tertiary alcohol was consumed. After drying, the olefinic products were separated by short-path distillation and isolated by GC to give two components in a 4:1 ratio. The major product was 1-isopropylcyclohexene (**9b**): 220 MHz NMR δ 0.90 (d, 6, J =

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6 Hz), 1.40–1.62 (m, 4), 1.9 (m, 4), 2.05 (septet, 1) and 5.25 ppm (s, 1); IR 3060, 1665, and 810 cm^{-1}. The minor product was isopropylidenecyclohexane (**8b**): NMR δ 1.2–1.7 (m, 12) and 1.8–2.3 ppm (m, 4).

1-Isopropylcycloheptene (9c) and Isopropylidenecycloheptane (8c).[20] These materials were prepared in an analogous manner from cycloheptanone in a 3:1 ratio and isolated by GC. The major product was 1-isopropylcycloheptene (**9c**): NMR δ 0.90 (d, 6, J = 6 Hz), 1.3–2.6 (m, 11) and 6.5 ppm (t, 1, J = 6 Hz); IR 3050, 1660, and 850 cm^{-1}. The minor product was isopropylidenecycloheptane (**8c**): NMR δ 1.2–1.7 (m, 14) and 1.8–2.3 ppm (m, 4).

1-Isopropylcyclopentene (9a) and Isopropylidenecyclopentane (8a).[20] In an analogous fashion cyclopentanone was converted to a 1:1 mixture of 1-isopropylcyclopentene (**9a**) and isopropylidenecyclopentane (**8a**) which was separated by GC. The former showed the following: NMR δ 1.05 (d, 6, J = 6 Hz), 1.4–2.6 (m, 5), and 5.17 ppm (br, s, 1); IR 3050, 1645, 810 cm^{-1}. The latter showed the following: NMR δ 1.6 (br, s, 10) and 2.1 ppm (m, 4).

(2-Methyl-1-propenyl)cyclopentane (11b). To a solution of 16.8 g (40 mmol) of isopropyltriphenylphosphonium iodide[21] in 400 mL of anhydrous ether under N_2 was added dropwise 19 mL (40 mmol) of 2.1 M n-butyllithium with stirring. The solution rapidly became blood red. After 2 h, a solution of 3.92 g (40 mmol) of cyclopentanecarboxaldehyde in 20 mL of ether was added in small portions. This caused the solution to reflux and become milky white. After several hours the reaction mixture was hydrolyzed by the addition of 10 mL of water, the solid was removed by filtration, and the ether layer was separated and dried. The solvent was removed through a Vigreux column and distillation gave 2.5 g (51%) of **11b**: bp 145–146 °C; NMR δ 0.9–2.0 (m, 14) including two closely spaced doublets (J = 1 Hz) at 1.6 ppm, 2.5 (m, 1) and 4.90 ppm (d of m, 1, J = 8, 1 Hz). Anal. Calcd for C_9H_{16}: C, 87.09; H, 12.90. Found: C, 87.0; H, 12.8.

(2-Methyl-1-propenyl)cyclohexane (11c).[22] An identical experiment using 4.4 g (40 mmol) of cyclohexanecarboxaldehyde gave 3.1 g (56%) of **11c**: bp 168–169 °C; NMR δ 0.8–2.3 (m, 17) including two closely spaced doublets (J = 1 Hz) at 1.6 ppm and 4.80 (1, d of m, J = 8, 1 Hz).

2-Methyl-2,3-octadiene (10b).[7] To a slurry of 0.5 g of lithium aluminum hydride in 20 mL of THF was added 0.6 g of iodide **1** in 5 mL of THF. After heating to reflux for 2 h the reaction was hydrolyzed by the addition of 0.6 mL of water followed by 1.8 mL of 15% NaOH solution and finally 1.8 mL of water. After filtration and drying, the solvent was removed by distillation through a Vigreux column and the residue was purified by GC to give **10b** as the only significant product: NMR (220 MHz) δ 0.89 (t, 3, J = 7 Hz), 1.32 (m, 4), 1.61 (d, 6, J = 3 Hz), 1.88 (m, 2) and 4.77 ppm (m, 1); IR 1975 cm^{-1}.

2-Methyl-2,3-nonadiene (10c). The reduction of iodide **2** in a similar manner in THF or ether gave **10c**: NMR δ 0.9 (m, 3), 1.3 (br, s, 6), 1.62 (d, 6, J = 3 Hz), 1.9 (m, 2) and 4.78 ppm (m, 1); IR 1969 cm^{-1}. Anal. Calcd for $C_{10}H_{18}$: C, 86.95; H, 13.05. Found: C, 86.8; H, 13.1.

2-Methyl-2,3-decadiene (10d). The reduction of iodide **3** in an analogous manner in ether solution gave **10d**: NMR δ 0.9 (m, 3), 1.3 (br, s, 8), 1.62 (d, 6, J = 3 Hz), 1.9 (m, 2), and 4.81 ppm (m, 1); IR 1986 cm^{-1}. Anal. Calcd for $C_{11}H_{20}$: C, 86.84; H, 13.16. Found: C, 86.8; H, 13.1.

Acid Isomerization of 10b. A mixture of 0.36 g of **10b** and two drops of concentrated sulfuric acid in 20 mL of THF was heated to reflux for 7 days. At the end of this time about 60% of the allene was isomerized to a mixture of three products in a ratio of 12:59:29. Dilute NaOH solution was added and the mixture was extracted with pentane. The extract was dried and concentrated by careful distillation and the major product was isolated by GC. It is assigned as *trans*-2-methyl-1,3-octadiene on the basis of its spectral properties: NMR (220 MHz) δ 0.85 (t, 3), 1.30 (m, 4), 1.75 (s, 3), 2.05 (m, 2), 4.70 (br, s, 2), 5.6 (d of t, 1, J = 15, 7 Hz) and 6.2 ppm (d, 1, J = 15 Hz); IR 3090, 1645, 1610, 970, 890 cm^{-1}; mass spectrum M^+ 138 (4%).

Tin Hydride Reduction of 4. To a solution of 0.77 g (4.1 mmol) of **4** in 60 mL of benzene at refulx was added dropwise 2.2 g (6.1 mmol) of Bu_3SnH and several milligrams of azobis[isobutyronitrile] (AIBN) in 60 mL of benzene over a 1.5-h period. The disappearance of starting bromide required several additional hours as followed by TLC. Analysis by GC indicated the formation of three products in a 45:4:51 ratio in a total yield of 90%. Most of the solvent was removed by distillation through a spinning band column. The product was obtained by distillation using n-decane as a chaser. The two major products were isolated by GC and identified as **8a** and **9a**, respectively, by comparison with authentic samples. The minor product was not isolated in sufficient quantity for characterization.

A second reaction was performed by adding 50 μL of **4** to 1 mL of Bu_3SnH containing several milligrams of AIBN and heating to 75 °C for 3 h. The product was collected in a dry ice trap by evacuating the system to 50 torr during the reaction followed by the addition of 1 mL of cyclohexane to the reaction mixture and subsequent distillation into the trap. Analysis of the distillate by GC showed a 17:39:42 mixture of **10a**:**8a**:**9a**. The minor product observed in the reaction performed in benzene solution was present as less than 2% of this mixture.

Tin Hydride Reduction of 1. To a solution of 2.5 g (10 mmol) of **1** in 150 mL of benzene at reflux was added dropwise 4.5 g (12.5 mmol) of Bu_3SnH in 150 mL of benzene over a 5-h period. TLC analysis at this point indicated the disappearance of starting iodide. Analysis by GC indicated three peaks in the ratio of 20:76:4 in a total yield of 80%. Most of the solvent was removed by careful distillation and ca. 1 mL of product of bp 84–86 °C (115 torr) was collected. GC analysis of this material indicated that the relative intensity of the first peak had diminished during processing. Isolation of these peaks by GC allowed the assignment of the first and third as **10b** and **8b**, respectively, by comparison with authentic samples. The second peak was shown to be a 35:65 mixture of two components by capillary GC. NMR (220 MHz) analysis of this mixture allowed assignment of the two peaks as **9b** and **11b**, respectively, by comparison with the spectra of authentic samples.

In a second experiment 90 mg of iodide **1** was added to 1 mL of Bu_3SnH causing a mildly exothermic product. The volatile product was collected in a dry ice trap under vacuum. Analysis by GC and NMR indicated **10b** as the only significant product.

Tin Hydride Reduction of 2. To a solution of 1.5 g (5.6 mmol) of **2** in 90 mL of benzene at reflux was added dropwise over 5.5 h a solution of 2.7 g (7.5 mmol) of Bu_3SnH in 90 mL of benzene. TLC analysis indicated the disappearance of starting iodide. Analysis by GC showed the presence of three peaks in a ratio of 60:23:17 in a total yield of 91%. The solvent was removed by careful distillation and a product fraction of bp 100–110 °C (130 torr) was obtained. The three peaks were isolated by GC. The first peak, which had decreased relative to the others during the isolation procedure, was shown to be allene **10c** by comparison with an authentic sample. Likewise the second peak was assigned as **11c**. The third peak appears to be predominately *trans*-2-methyl-2,4-nonadiene: IR 3030, 1660, 1620, 1040, 990, and 960 cm^{-1}; NMR δ 0.9 (m, 3), 1.3 (m, 4), 1.7 (br s, 6), 2.0 (m, 2), 5.3 (d of t, 1, J = 14, 7 Hz), 5.6 (d, 1, J = 11 Hz), and 6.0 (m, 1). The cis isomer may also be present in small quantities as indicated by extra peaks in the vinyl region of the NMR spectrum.

In a second experiment 100 mg of **2** was added to 700 mg of liquid Bu_3SnH at room temperature. Analysis by TLC after 8 h indicated the absence of starting iodide. GC showed **10c** as the only significant product.

Tin Hydride Reduction of 3. To a solution of 1.62 g (5.8 mmol) of **3** in 100 mL of benzene at reflux was added dropwise over 4 h 2.60 g (7.2 mmol) of Bu_3SnH in 70 mL of benzene. TLC analysis at this point indicated the absence of starting material. GC showed three peaks in a ratio of 90:3:7. Most of the solvent was removed under vacuum and the residue was chromatographed over silica gel using pentane as eluent to give 0.67 g (75%) of hydrocarbon product. The components were isolated by preparative GC. The major product was assigned as **10d** by comparison with an authentic sample. The second peak is tentatively assigned as *trans*-2-methyl-1,3-decadiene on the basis of the near identity of the characteristic vinyl region in its NMR spectrum [δ 0.9 (m, 3), 1.3 (br s, 8), 1.7 (br s, 6), 2.1 (m, 2), 4.8 (br s, 2), 5.6 (d of t,

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1, J = 15, 7 Hz) and 6:2 (d, 1, J = 15 Hz)] with that of its lower homologue described above. Analytical GC indicates two poorly resolved components in a 4:1 ratio for the third peak. These are tentatively identified as the isomeric 2-methyl-2,4-decadienes: IR 3020, 1655, 1620, 1080, 970, 940, 850 cm^{-1}; ^1H NMR δ 0.9 (m, 3), 1.2 (br s, 8), 1, 7 (br s, 6), 2.0 (m, 2), 5.5 (d of t, 1, J = 15, 7 Hz), 5.7 (d, 1, J = 11) and 5.9–6.3 (m, 1). These values are also very similar to those of the lower homologue described above.

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Registry No. 1, 90047-74-8; 2, 90047-75-9; 3, 90047-76-0; 4, 90047-77-1; **6a**, 90047-78-2; **6b**, 60431-22-3; **6c**, 90047-79-3; 7, 2806-55-5; **8a**, 765-83-3; **8b**, 5749-72-4; **8c**, 7087-36-7; **9a**, 1462-07-3; **9b**, 4292-04-0; **9c**, 17257-36-2; **10b**, 42192-42-7; **10c**, 59578-60-8; **10d**, 90047-80-6; **11b**, 53366-57-7; **11c**, 89656-98-4; **12a**, 90047-81-7; **12b**, 90047-82-8; **12c**, 90047-83-9; **12d**, 90047-84-0; CH_2=C=C$(CH_3)_2$, 598-25-4.

Molecular Orbital Calculations and ^{13}C NMR Studies To Explain a Regiospecific Demethylation of 3-Alkyl-1,2-dimethoxybenzenes

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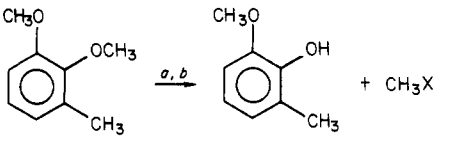
This study was performed to explain a regiospecific demethylation of 3-alkyl-1,2-dimethoxybenzenes. PRDDO–MO calculations show that the low-energy conformation of the carbon of a methoxy group having two ortho neighbors on a benzene ring is located out of the plane of the aromatic ring, whereas a methoxy group with only one ortho neighbor executes restricted rotation in the plane of the ring. The carbon portion of the methoxy group is turned away from the neighboring substituent. These calculations also show that the atomic charge on the oxygen atom in the former case exceeds that in the latter. The carbon of a methoxy group with two ortho neighbors yields ^{13}C NMR T_1 relaxation times longer than those with only one ortho neighbor, also suggesting that the methoxy group with two ortho neighbors is crowded out of the plane of the aromatic ring. ^{13}C NMR chemical shifts of these ortho-substituted methoxybenzenes did not correlate well with shifts predicted from published additive parameters; this again suggests an unusual methoxy group orientation and distribution of electrons. The forced rotation of a methoxy group out of the plane of the benzene ring diminishes the release of electrons from the methoxy group to the benzene ring. The resulting higher atomic charge on the oxygen and the orientation of the oxygen orbitals facilitate complexation with Lewis acids and methoxy group cleavage.

Our recent demonstration of the regiospecific cleavage of 3-alkyl-1,2-dimethoxybenzenes by boron tribromide and iodotrimethylsilane to 2-alkyl-6-methoxyphenols,[2a] along with earlier observations[2b-d] of similar effects, prompted a detailed analysis of the conformational orientation of the methoxy groups to elucidate the origin of this regiospecificity. Studies of Dreiding models suggested that the orientation of the p orbitals of the respective oxygen atoms is the source of this behavior and that providing or blocking access to them by Lewis acids during complexation and/or attack of nucleophiles on methoxy carbon is the key to the course of the reaction and the regiospecificity shown in Scheme I.

The Halgren–Lipscomb PRDDO program[3] was obtained and atomic charges for various nuclei at different dihedral angles and the total energy of each molecule were calculated. PRDDO is intermediate in complexity between CNDO/INDO and ab initio calculations, as it retains all three- and four-centered integrals. PRDDO is comparable in accuracy to the more sophisticated STO-3G calculations with respect to optimal geometries and requires computer costs only 2–3 times that of the less accurate CNDO/INDO computations.[3b,c]

Scheme I



3b

[a] Iodotrimethylsilane or boron tribromide. [b] H_2O.

Tables I–V of calculated atomic charges and dipole moments were developed. These are available as supplementary material and include information about the monomethoxybenzenes **1a–e** and **2a** (Table I) and the dimethoxybenzenes **3b** (Table II) and **3e** (Table III) as well as 4,5-dimethoxyindan (**4**) (Table IV). A summary of PRDDO electron densities and calculated dipole moments at minimum energy for **3b**, **3c**, **3d**, **3e**, and **4** is presented in Table V.

An appreciation of the relative magnitudes of the calculated rotational barrier energies for **1a**, **1b**, and **2a** can be gained from Figure 1. While the calculated barrier for **1a** is 1.50 kcal/mol, it must be remembered that these calculations are uncertain by at least this amount. Hence, this barrier should be regarded as merely low and the motion of the methoxy group as only slightly hindered at room temperature. On the other hand, the location of one methyl group ortho to methoxy, as in **1b**, effectively excludes the methoxy group from an angular region ±60° on either side of the methyl group. The addition of two ortho

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