reaction. No aldehyde could be isolated, but copious amounts of 4-(dimethylamino)pyridine were recovered upon workup, apparently due to ligand exchange.

Manganese dioxide has been widely used for the selective oxidation of allylic and benzylic alcohols. Unfortunately, this specially prepared reagent must be used in large excess, and long reaction times are often necessary for successful oxidations.[9] The recently described bis(tetrabutylammonium)dichromate[10] shows selectivity in benzylic and allylic oxidations, but workup is complicated and no details of oxidation of complex multifunctional molecules have been reported. The ready preparation of 4-(dimethylamino)pyridinium chlorochromate, its selectivity, and the ease of using this reagent indicate that **3** may prove to be a useful alternative to other reagents in oxidations of complex allylic and benzylic alcohols.[11] Investigations into the reasons for the observed selectivity and into the usefulness of other ligands in selective oxidations are currently in progress.[12]

Acknowledgment. We thank Reilly Tar and Chemical Corp. for providing 4-(dimethylamino)pyridine and Professor Paul Vouros for providing low-resolution mass spectra. We also gratefully acknowledge the helpful comments of Professor Harold Kwart.

Registry No. **3**, 81121-61-1; **4**, 38628-53-4; **5**, 81121-62-2; **6**, 3917-39-3; **7**, 3917-41-7; **8**, 81176-75-2; **9**, 58-22-0; **10**, 63-05-8; **11**, 81176-76-3; **12**, 564-35-2; benzyl alcohol, 100-51-6; 2-thiophenemethanol, 636-72-6; *o*-methylbenzyl alcohol, 89-95-2; *p*-methoxybenzyl alcohol, 105-13-5; 5-benzodioxolemethanol, 495-76-1; *p*-nitrobenzyl alcohol, 619-73-8; 3,4-dimethoxybenzyl alcohol, 93-03-8; *p*-chlorobenzyl alcohol, 873-76-7; 3,4,5-trimethoxybenzyl alcohol, 3840-31-1; *p*-(benzyloxy)benzyl alcohol, 836-43-1; *p*-isopropyl benzyl alcohol, 536-60-7; 2-pyridinemethanol, 586-98-1; hex-zen-1-ol, 928-95-0; 3-phenylprop-2en-1-ol, 4407-36-7; non-2-en-1-ol, 31502-14-4; 2-methyloct-2-en-1-ol, 33965-55-8; geraniol, 106-24-1; 4-(tetrahydropyranyloxy)-but-2-en-1-ol, 58201-77-7; 4-hydroxybut-2-enyl benzoate, 81121-63-3; 2-cyclohexen-1-ol, 822-67-3; benzaldehyde, 100-52-7; 2-thiophenecarboxaldehyde, 98-03-3; *o*-methylbenzaldehyde, 529-20-4; *p*-methoxybenzaldehyde, 123-11-5; 5-benzodioxolecarboxaldehyde, 120-57-0; *p*-nitrobenzaldehyde, 555-16-8; 3,4-dimethoxybenzaldehyde, 120-14-9; *p*-chlorobenzaldehyde, 104-88-1; 3,4,5-trimethoxybenzaldehyde, 86-81-7; *p*-(benzyloxy)benzaldehyde, 4397-53-9; *p*-isopropylbenzaldehyde, 122-03-2; 2-hexenal, 505-57-7; 3-phenyl-2-propenal, 104-55-2; 2-nonenal, 2463-53-8; 2-methyl-2-octenal, 73757-27-4; geranial, 141-27-5; 4-(tetrahydropyranyloxy)-2-butenal, 78008-26-1; 4-(benzyloxy)-2-butenal, 81121-64-4; 2-cyclohexenone, 930-68-7.

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[9] Reference 2a, pp 265–267.

[10] Santaniello, E.; Ferraboschi, P. *Synth. Commun.* **1980**, *10*, 75.

[11] For example, oxidations of compound **6** with manganese dioxide required very long reaction times, affording the aldehyde as a mixture of cis and trans isomers, often in low yield. Oxidation of geraniol with bis(tetrabutylammonium) dichromate affords a mixture of geranial and neral (9:1).

[12] It appears that chromate esters form in high yield even in the cases of primary and secondary alcohols and that differential breakdown of the chromate esters leads to the observed selectivity. Most simply, changing ligands on chromium changes its oxidation potential and, therefore, its reactivity.

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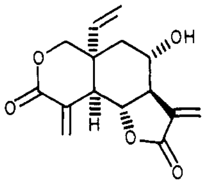
Received February 18, 1982

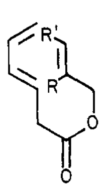
Stereocontrol in the Intramolecular Diels–Alder Reaction. 4. A Remarkable Effect of Overlap Requirements in the Connecting Chain[1]

Summary: The intramolecular Diels–Alder cyclizations of two triene diesters derived from (*E*)-3,5-hexadienoic acid have been investigated. The cyclizations proceed remarkably sluggishly and only after double-bond isomerization to the sorbate derivative has occurred. The reasons behind this unusual behavior were investigated, and evidence points strongly to the effects of overlap requirements of the ester linkage in the transition state as the major factor.

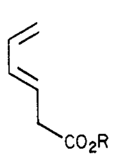
Sir: As part of a synthetic approach to cis bicyclic δ-lactones related to vernolepin (**1**), we had occasion to investigate the thermal cyclization of triene ester **2** which was readily prepared from (*E*)-3,5-hexadienoic acid (**3**)[2] and methyl 2-(hydroxymethyl)acrylate (**4**)[3] by coupling with DCC/py (1.02 equiv) in ether at 0 °C for 12 h (78% yield).



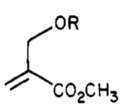
1



2, R = CO_2CH_3; R' = H
9, R = H; R' = $CO_2C_2H_5$



3, R = H
5, R = CH_3



4, R = H
6, R = Ac

However, in spite of the apparently good transition-state geometry for cycloaddition available to **2**,[4] thermolysis of **2** at a variety of temperatures up to 220 °C in high-boiling solvents in the presence of radical inhibitors afforded either recovery of **2** or polymeric products resulting from slow degradation of the dienophile segment in **2**.[5] To determine whether some inherent reactivity factor was preventing successful cycloaddition, we examined the analogous bimolecular reaction of methyl (*E*)-3,5-hexadienoate (**5**) and methyl (acetoxymethyl)acrylate (**6**). It was found that this bimolecular reaction occurred slowly but quite cleanly (110 °C/96 h) to afford a mixture of two δ-lactones **7** and **8** (2:1) after ring closure ((1) $NaOCH_3/CH_3OH$, room temperature, (2) 10% HCl/CH_3OH) in 70% yield. The structure and stereochemistry of **7** and **8** were established by correlation with authentic materials.[6] The surprising ease with which the bimolecular reaction took place suggested some significant energy barrier to cyclization was present in **2** as the result of electronic or steric interactions among the atoms in the connecting chain or of these atoms with the diene or dienophile segments of the substrate. The

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[1] Initial stages of these studies were conducted at Wayne State University, Detroit, Michigan.

[2] (a) Prepared in 69% yield by quenching the dianion prepared from sorbic acid (LDA (2.2 equiv) and HMPA in THF–hexane at 0 °C) with 6 N HCl; (b) J. B. Medwid, Ph.D. Dissertation, Wayne State University, Detroit, MI, 1980.

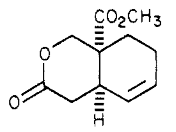
[3] Rosenthal, R. W.; Schwartzman, L. H.; Greco, N. P.; Proper, R. *J. Org. Chem.* **1963**, *28*, 2835.

[4] Examination of molecular models of **2**, focusing on the reacting centers, shows that good orbital overlap is possible at the appropriate trajectory angles of approach (75°) as judged from calculated values; E. Ciganek, private communication. We thank him for making his results available to us prior to publication.

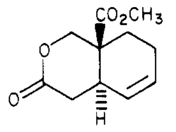
[5] NMR spectra of the polymerized products suggested strongly that bimolecular Diels–Alder reactions were not the mechanism of polymerization. Diene resonances remained relatively intact; however, the characteristic methylene resonances of the dienophile were completely absent.

0022-3263/82/1947-1789$01.25/0

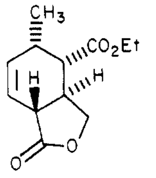
single steric factor which conceivably was responsible appeared to be the location of the dienophile activating group which was situated in the more congested angular position. We, therefore, prepared the related triene diester **9** by base-promoted esterification of **3** with ethyl 4-bromocrotonate (NaH/DMF) in 80% yield. As before, thermolysis of **9** at temperatures up to 200 °C afforded, at most, trace amounts of cycloadducts. However, further investigation of this reaction revealed that heating **9** in toluene at temperatures of 220–225 °C (4 h) in a sealed tube (Ar) provided a mixture (~8:1) of two cycloadducts (~40% yield). The structure of the major adduct (mp 62–64 °C) was assigned as the trans butyrolactone **10a** on the basis of 400-MHz NMR spectral data.[7] The production of the rearranged γ-butyrolactones **10a** and **10b** rather than the expected δ-lactone **11** was unexpected and rearrangement in this context is unprecedented to our knowledge.[8,9] The structures of **10a** and **10b** were further established by the isolation of the identical cycloadducts (mp, IR, NMR) as the cyclization product (9:1 trans/cis) in 79% yield upon thermolysis at 135 °C (15.5 h) of triene **12** prepared from sorbic acid and ethyl 4-bromocrotonate (NaH/DMF; 50%).



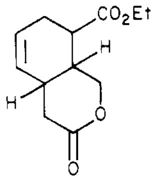
7



8

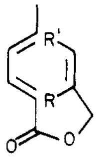


10a, R = β-H
b, R = α-H

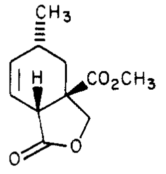


11

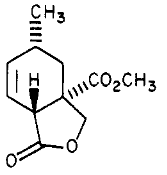
Reinvestigation of the cyclization of triene **2** under much more vigorous conditions also proved fruitful. Thermolysis of **2** in toluene at 295 °C for 4 h (sealed tube) afforded the analogous rearranged γ-butyrolactone adducts **13** and **14** (63:37) in 15% yield.[7] The structures of **13** and **14** were again established by isolation of nearly the same mixture of **13** and **14** (55:45) upon thermolysis of triene diester **15** at 250 °C (4 h).[7] Triene diester **15** (mp 48–49 °C) was prepared as before by coupling (NaH/ether/room temperature) of sorbic acid and methyl 2-(bromomethyl)acrylate (65%).



12, R = H;
R′ = CO_2Et
15, R = CO_2CH_3;
R′ = H



13

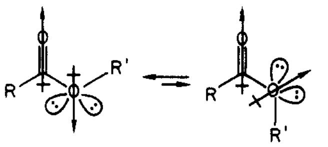


14

The formation of essentially identical product mixtures from **2** and **15**, as well as **9** and **12**, strongly implies that double-bond rearrangement must be the rate-determining step in the process of cyclization of **2** and **9** by whatever mechanism it occurs.[10] Since both **2** and the relatively unencumbered **9** show identical behavior, steric effects were excluded as the primary factor, and our attention then centered upon the electronic requirements of the ester linkage.

The observation that overlap requirements of groups within the connecting chain are important in determining the outcome of an intramolecular cycloaddition was first made by Oppolzer.[11] In the diene amide systems examined in these studies, significant changes in the observed stereoselectivity of the cycloadditions were noted which were apparently due to the location of the amide carbonyl either within or external to the connecting chain.

The propensity of esters to exist nearly totally in the transoid geometry (eq 1) due primarily to dipole repulsions



(1)

is well-known.[12] In the s-trans conformation, the diene and dienophile are not properly disposed to cyclize. However, the barrier to rotation about the ester C–O bond (≤~10

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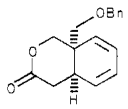
(6) These experiments were performed by Jeffrey B. Medwid. The comparison was conducted by correlation with diene lactone i



i

whose structure and stereochemistry were established by X-ray analysis of a derivative: cf. Boeckman, R. K., Jr.; Ramaiah, M.; Medwid, J. B. *Tetrahedron Lett.* **1977**, 4485 and ref 2b.

(7) The spectral data are as follows. **10a**: IR (CCl_4), 1775, 1720 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 6.00 (m, 1), 5.86 (dd, J_1 = 9.8 Hz, J_2 = 4.4 Hz, 1), 4.47 (dd, J_1 = 9.8 Hz, J_2 = 5.9 Hz, 1), 4.23 (m, 2), 4.12 (d, J = 10.3 Hz, 1), 3.28 (m, 1), 3.05 (m, 1), 2.79 (m, 1), 2.70 (dd, J_1 = 12.2 Hz, J_2 = 4.9 Hz, 1), 1.30 (t, J = 7.3 Hz, 3), 0.90 (d, J = 7.3 Hz, 3). **10b**: IR (CCl_4) 1775, 1720 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.90 (m, 1), 5.73 (d, J = 9.5 Hz, 1), 4.32 (dd, J_1 = 9.5 Hz, J_2 = 6 Hz, 1), 4.25 (q, J = 6 Hz, 2), 4.13 (d, J = 9.5 Hz, 1), 3.23 (m, 1), 2.91 (m, 1), 2.45 (m, 1), 2.10 (t, J = 12.3 Hz, 1), 1.29 (t, J = 6 Hz, 3), 1.05 (d, J = 6 Hz, 3). **13**: IR (film) 1790, 1750 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.83 (d, J = 10 Hz, 1), 5.76 (dt, J_1 = 10.1 Hz, J_2 = 2.4 Hz, 1), 4.51 (d, J = 9.4 Hz, 1), 4.17 (d, J = 9.4 H, 1), 3.78 (s, 3), 3.54 (m, 1), 2.30 (m, 1), 2.01 (dd, J_1 = 14.1 Hz, J_2 = 5.8 Hz, 1), 1.65 (dd, J_1 = 14.1 Hz, J_2 = 9.7 Hz, 1), 1.05 (d, J = 7.1 Hz, 3). **14**: IR (film) 1790, 1750 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.85 (dt, J_1 = 10 Hz, J_2 = 4.6 Hz, 1), 5.75 (d, J = 9.1 Hz, 1), 4.28 (d, J = 9.2 Hz, 1), 4.09 (d, J = 9.2 Hz, 1), 3.77 (s, 3), 3.57 (s (br), 1), 2.23 (m, 2), 1.34 (dd, J_1 = 12.7 Hz, J_2 = 1.3 Hz, 1), 1.03 (d, J = 6.9 Hz, 3). **19**: IR (CCl_4) 1728, 1683 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.64 (d, J = 7.8 Hz, 1), 5.52 (d, J = 7.8 Hz, 1), 3.73 (d, J = 11.4 Hz, 1), 3.64 (s, 3), 3.57 (d, J = 11.4 Hz, 1), 3.49 (m, 1), 2.48 (s, 1), 2.14–1.40 (m, 7). **21**: IR (film) 1728, 1674, 1643 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.67 (s, 2), 4.17 (q, J = 9 Hz, 2), 3.86 (dt, J_1 = 12 Hz, J_2 = 4.8 Hz, 1), 3.81 (dd, J_1 = 12 Hz, J_2 = 4.8 Hz, 1), 3.55 (dd, J_1 = 12 Hz, J_2 = 4.8 Hz, 1), 3.43 (dt, J_1 = 12 Hz, J_2 = 4.8 Hz, 1), 2.89 (q, J = 9 Hz, 1), 2.42–2.12 (m, 4), 2.00 (m, 1), 1.68–1.50 (m, 3), 1.23 (t, J = 9 Hz, 3). **22**: IR (film) 1725, 1695, 1645 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.65 (m, 1), 5.50 (d, J = 9.5 Hz, 1), 4.14 (dq, J = 7.2 Hz, 2), 4.02 (dd, J_1 = 12 Hz, J_2 = 5.4 Hz, 1), 3.88 (dd, J_1 = 12 Hz, J_2 = 5.4 Hz, 1), 3.47 (dt, J_1 = 12.9 Hz, J_2 = 3 Hz, 1), 3.18 (t, J = 11.4 Hz, 1), 2.45–2.28 (m, 3), 2.02 (t (br), 1), 1.76 (dq, J_1 = 6.6 Hz, J_2 = 5.4 Hz, 1), 1.65 (d (br), J = 16.8 Hz, 1), 1.45 (dq, J_1 = 12 Hz, J_2 = 5.4 Hz, 1), 1.27 (t, J = 7.2 Hz, 3). **24**: IR (film) 1720, 1712 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.63 (m, 1), 5.50 (dd, J_1 = 10.5 Hz, J_2 = 3 Hz, 1), 3.77 (s, 3), 3.23 (s (br), 1), 2.64 (dd, J_1 = 15 Hz, J_2 = 6 Hz, 1), 2.40 (dt, J_1 = 12, J_2 = 6 Hz, 1), 2.32–1.77 (m, 8). **25**: IR (film) 1721, 1709 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 5.66 (m, 1), 5.50 (t, J = 11.4 Hz, 1), 3.75 (s, 3), 3.14 (t, J = 14.7 Hz, 1), 2.41–2.04 (m, 9), 1.68 (dt, J_1 = 16.8 Hz, J_2 = 6 Hz, 1).

(8) (a) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (b) Oppolzer, W. *Synthesis* **1978**, 793. (c) Oppolzer, W. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 10. (d) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (e) Carlson, R. G. *Ann. Rep. Med. Chem.* **1974**, *9*, 270.

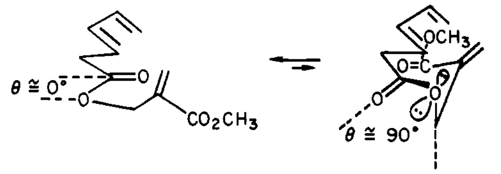
(9) The cyclization of other esters and amides is well precedented: (a) Ciganek, E. *J. Am. Chem. Soc.* **1981**, *103*, 6261. (b) White, J. D.; Sheldon, B. D. *J. Org. Chem.* **1981**, *46*, 2273. (c) Martin, S. F.; Tu, C.; Chou, T. *J. Am. Chem. Soc.* **1980**, *102*, 5274.

(10) This result is inferred from the apparent relative rates of cyclization as judged from the reaction temperatures required.

(11) (a) Oppolzer, W.; Frostl, W. *Helv. Chim. Acta* **1975**, *58*, 590. (b) Oppolzer, W.; Keller, K. *J. Am. Chem. Soc.* **1971**, *93*, 3836.

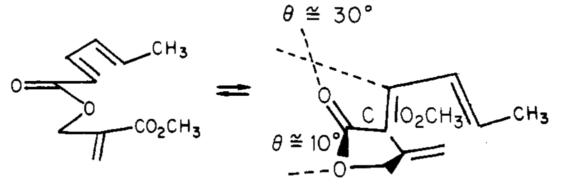
(12) (a) Nakanishi, H.; Oki, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2558. (b) Wennerstrom, H.; Forsen, S.; Roos, B. *J. Phys. Chem.* **1972**, *76*, 2436. (c) Nakanishi, H.; Fujita, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 214. (d) Wilmshurst, J. K. *J. Mol. Spectrosc.* **1957**, *1*, 201.

kcal/mol) is sufficiently low so as to rule out this equilibrium effect as the cause of the apparently unusually high activation free energy (ΔG^{*}) for cyclization, on the basis of the Curtin–Hammet principle.[13] These facts suggest that the high kinetic barrier to cyclization is the result of electronic demands of the ester in the transition state. Closer examination of the conformations of 2 and 9 in the approximate geometry of the transition state reveals that the ester linkage is effectively totally uncoupled in this conformation. This uncoupling is reflected in an approximately 90° dihedral angle between the carbonyl π system and the lone-pair orbitals on the adjacent oxygen atom, preventing overlap.[14]



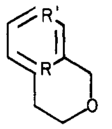
(2)

It is significant, also, that cyclization of both **12** and **15** proceeds at considerably lower temperatures than **2** and **9**.[15] This result can be rationalized by consideration of the analogous transition-state conformations for **12** and **15** (eq 3) which indicates that (1) conjugation of the carbonyl with the diene system reduces the electronic demand for overlap with the oxygen of the ester in the transition state, (2) the conformation required does not result in significant loss of overlap with the diene π system, and (3) the decoupling of the ester oxygen is not as complete as for **2** and **9**.[16-18] Thus, **12** and **15** must still pay the price, in energy terms, for assuming the s–cis conformation but are not energetically prevented from reaching the required transition-state geometry due to the overlap requirements of the ester.[19]

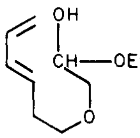


(3)

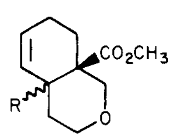
We have performed two sets of experiments which support the idea that overlap requirements of the ester in the transition state are responsible for the anomalous behavior of **2** and **9**. We have prepared the triene esters **16** and **17**, the former by coupling of **6** with (*E*)-3,5-hexadien-1-ol (DMAP/CH_2Cl_2; 50%) via addition–elimination and the latter by reaction of **18** with $(EtO)_2P(O)CH_2CO_2Et$ (3 equiv) and NaH in THF (58%).[20]



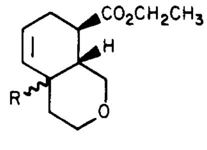
16, R = CO_2CH_3; R' = H
17, R = H; R' = $CO_2C_2H_5$



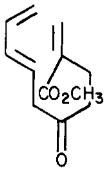
18



19, R = β-H (cis)
20, R = α-H (trans)



21, R = β-H (cis)
22, R = α-H (trans)



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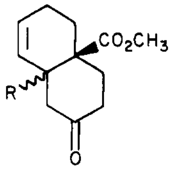

24, R = β-H (cis)
25, R = α-H (trans)

If overlap requirements of the ester were the primary factor, **16** and **17** would be expected to behave normally, and that is indeed the case. Thermolysis of **16** and **17** at 170 °C for 18–22 h (not optimized) affords exclusively the unrearranged cycloadducts **19–20** (70:30) and **21–22** (40:60) in good yields (50% and 86%, respectively).[7] Authentic rearranged materials were prepared to assure that no rearrangement was detectable.[21]

One final point which had to be addressed concerns the ease of isomerization of the β,γ-carbonyl system under the reaction conditions. To test this question, we prepared trienone ester **23**[22] and subjected it to thermolysis at 170 °C (22 h) to afford exclusively octalone products **24–25** (75:25; 50% yield).[7,23] No rearranged cycloadducts were detected by NMR (400 MHz).

Therefore, in these systems, at least, the presence and location of heteroatoms in the connecting chain and overlap requirements of these groups can have a substantial impact upon the rate of reaction and product distribution resulting from intramolecular cycloaddition.

Further investigations of the factors influencing re-

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[13] Dale, J. "Stereochemistry and Conformational Analysis"; Verlag Chemie; New York, 1978; p 84.

[14] The conformation required for cyclization appears to be that corresponding to the transition state for the ester C–O bond rotation.

[15] These data suggest a significantly lower ΔG^{*} for cyclization of **12** and **15**, reflecting a change in the transition-state geometry. This is in spite of the expected increase in ΔG^{*} due to an increase in the HOMO–LUMO gap as a result of carbonyl conjugation with the diene segment in **12** and **15**.

[16] Deviations of as much as 30° can be tolerated with little or no loss in stabilization due to disruption of overlap.

[17] In this case, molecular models suggest that the dihedral angle is approximately 10° between the carbon π system and oxygen lone-pair orbitals.

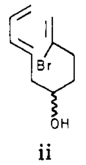
[18] Jackman, L. M. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Ed.; Academic Press: New York, 1975; p 223.

[19] The overlap requirements of conjugated systems are substantially less (3–4 kcal/mol) as judged from the change in rotational barrier in related amide systems upon conjugation, since the diene system serves to assume part of the stabilization of the carbonyl group as the system approaches the transition state.[18] The lower bound of the magnitude of the overlap requirement in these systems is estimated to be ~4 kcal/mol on the basis of the relative rate of isomerization vs. cyclization of the isomerized system.

[20] Hemiacetal **18** was prepared from (*E*)-3,5-hexadiene-1-ol by alkylation of the derived lithium salt with bromoacetaldehyde diethyl acetal in DMF (55%) and partial hydrolysis with HCl in aqueous THF (58%).

[21] The analogous substrates were prepared from sorbyl alcohol and cyclized. None of the cycloadducts prepared in this manner were detectable by VPC in the crude reaction mixtures derived from **16** and **17**.

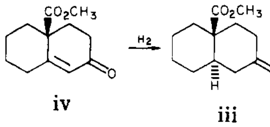
[22] Substrate **23** was prepared by condensation of (2,4-pentadienyl)triphenyltin and 4-bromo-4-pentenal in the presence of $TiCl_4$ (40%) to



ii

afford ii, protection of the alcohol (TBSCl/imidazole; 78%), carbomethoxylation with $Ni(CO)_4$ in methanol/$NaOCH_3$ (72%), hydrolysis (HCl), and Jones oxidation (50%).

[23] The structures of **24** and **25** were established by spectroscopic means (400-MHz NMR) as well as reduction of **24** and **25** (H_2, Pd/C) and comparison of the resulting decalones by VPC with the known trans decalone iii prepared by reduction of the octalone iv.



iv iii

activity and stereocontrol in the intramolecular Diels–Alder reaction are currently underway and will be the subject of forthcoming reports from these laboratories.

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Registry No. 2, 81095-98-9; **3**, 32775-95-4; **4**, 15484-46-5; **5**, 32775-94-3; **6**, 30982-08-2; **7**, 81095-99-0; **8**, 81096-00-6; **9**, 81096-01-7; **10a**, 81096-02-8; **10b**, 81096-03-9; **12**, 81096-04-0; **13**, 81096-05-1; **14**, 81096-06-2; **15**, 81096-07-3; **16**, 81096-08-4; **17**, 81096-09-5; **18**, 81096-10-8; **19**, 81096-11-9; **20**, 81096-12-0; **21**, 81120-64-1; **22**, 81096-13-1; **23**, 81096-14-2; **24**, 81096-15-3; **25**, 81096-16-4; ii, 81096-17-5; ethyl (*E*)-4-bromocrotonate, 19041-17-9; sorbic acid, 110-44-1; methyl 2-(bromomethyl)acrylate, 4224-69-5; 3,5-hexadien-1-ol, 5747-07-9; bromoacetaldehyde diethyl acetal, 2032-35-1; (2,4-pentadienyl)triphenyl tin, 81096-18-6; 4-bromo-4-pentenal, 36884-29-4.

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[24] (a) Fellow of the A. P. Sloan Foundation, 1976–1980. (b) Research Career Development Awardee (CA-00702), 1976–1980.

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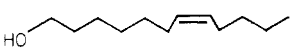
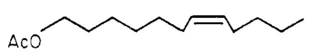
Pheromone Synthesis via Organoboranes: A Stereospecific Synthesis of (*Z*)-7-Alken-1-ols

Summary: Treatment of *trans*-1-alkenylborepanes, obtained via monohydroboration of 1-alkynes with borepane, with iodine in the presence of a base results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing intermediates containing the eight-membered borocane moiety, which undergoes a rapid deiodoboronation to afford the (*Z*)-7-alkenyl-1-boronate esters. These boronate esters on oxidation produce (*Z*)-7-alken-1-ols, providing a general, one-pot, and stereospecific synthesis of (*Z*)-7-alken-1-ols.

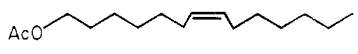
Sir: The synthesis[1] of unsaturated alcohols has attracted considerable attention of organic chemists in recent years because such alcohols[2,3] and their acetates[2,4] are known to be insect sex attractants. For example, (*Z*)-7-dodecen-1-ol (**1**) is the pheromone of the male moths of lepidoptera, *Raphia frater* Grt (Noctuidae),[3] and (*Z*)-7-dodecen-1-yl acetate (**2**) is the sex attractant of soybean loopers, *Pseudoplusia includens* (Walker),[5] and also of cabbage looper, *Trichoplusia ni* (Hübner).[6] (*Z*)-7-Tetradecen-1-yl acetate (**3**) is the phermone of the *Amathes c-nigrum* found both in Japan[7] and in Germany.[8] We now report a general, one-pot, and stereospecific synthesis of (*Z*)-7-alken-1-ols, thus providing a simple and very convenient route to the synthesis of pheromones **1**, **2**, and **3** via organoboranes.



1

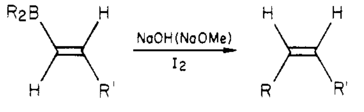


2

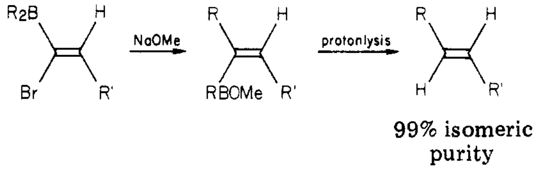


3

Organoboranes play an important role in bringing latitude to organic synthesis.[9] Highly stereospecific synthesis of cis[10] (eq 1) and trans[11] (eq 2) alkenes via organoboranes is well documented.

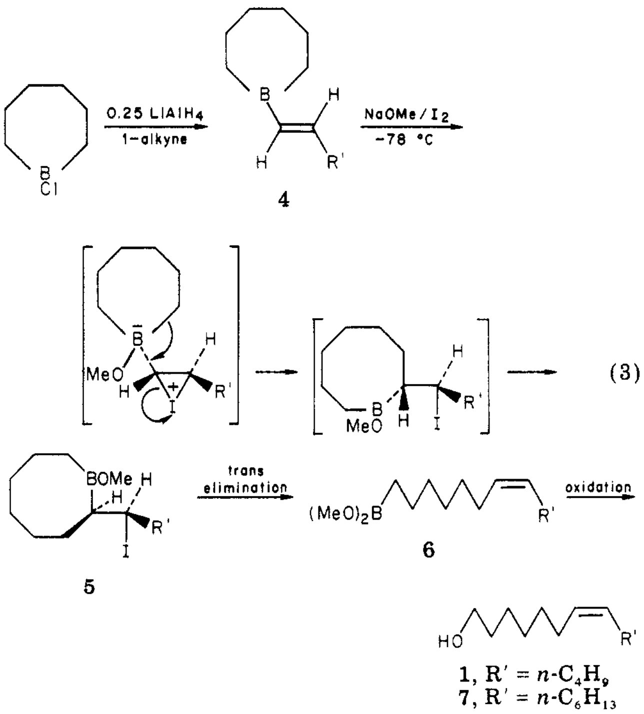


(1)



(2)

It appeared to us that the iodination of the *trans*-1-alkenylborepanes **4**, obtained via the monohydroboration of 1-alkynes with borepane, in the presence of a base should provide (*Z*)-7-alken-1-ols (eq 3). Accordingly, we examined this reaction sequence as a potential route for the synthesis of (*Z*)-7-alken-1-ols.



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