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1,3-Oxidative Rearrangements of Dienols§[1]

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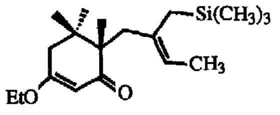
Summary: Oxidation of 1-vinyl-2-cycloalken-1-ols with PDC regiospecifically affords conjugated dienones in moderate to good yields.

The intramolecular addition of allylsilanes to conjugated dienones can be used to efficiently construct a wide variety of polycyclic systems.[2,3] However, on occasion we have been unable to prepare conjugated dienones *via* the addition of vinylic nucleophiles to α',α'-dialkyl-3-ethoxy-cycloalkenones.[4] For example, enone **1** proved inert to attack by vinyllithium (**4**) despite vigorous conditions [five equivalents of **4**, refluxing THF, 30 h], and moreover α-carbomethoxyvinylcuprate,[5] 4-chloro-2-lithio-1-butene,[6] and the lithium enolate of methyl β-(dimethylamino)-propionate[7] all failed to add to enones **2** or **3** (shown below). These additions failed presumably due to the modest reactivity of vinylogous esters **1**-**3** for 1,2-addition as well as steric factors.



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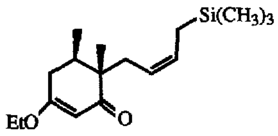

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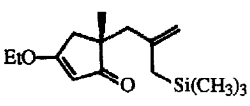
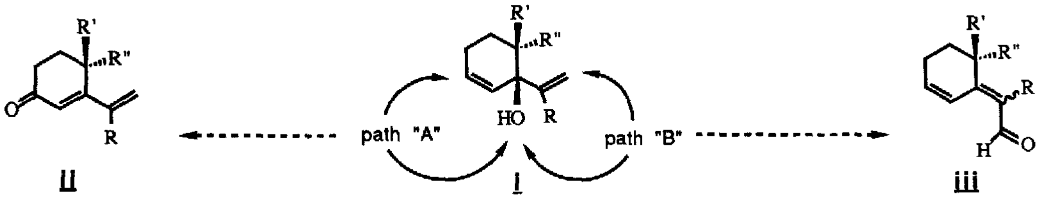


3

We speculated that functionalized dienones, such as **ii**, could be prepared via the oxidative rearrangement of bis-allylic tertiary alcohols (cf. **i**, Eq. 1). The requisite carbinols could be synthesized by addition of vinylic nucleophiles to the appropriate cycloalkenone. We hoped that the greater reactivity of enones for 1,2-addition would overcome the difficulties we encountered with less reactive vinylogous esters. Although CrO_3 and its less acidic derivatives, pyridinium chlorochromate (PCC) and pyridinium dichromate (PDC), have been used to oxidize tertiary allylic alcohols in numerous syntheses,[8,9] the oxidation of dienols such as **i** was limited to a single example which did not address the is-

Equation 1



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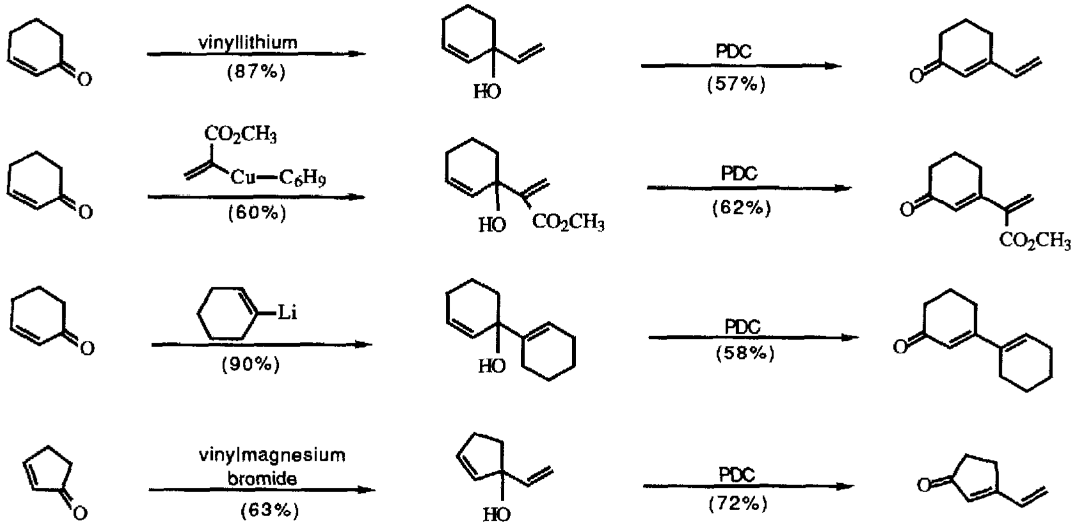
§ *Dedicated to Professors N. L. Allinger and R. K. Hill on the occasion of their 60th birthdays.*

sue of regioselectivity.[10] Our need for alternative routes to prepare conjugated dienones prompted us to make and oxidize analogs of **i**.[11]

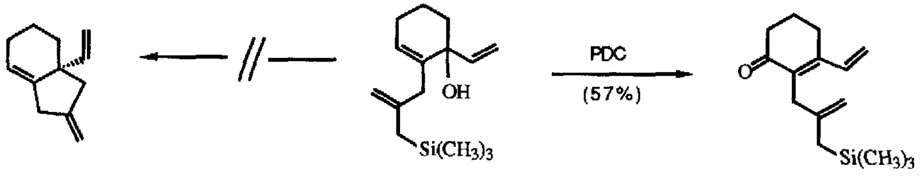
The regiospecificity of this reaction was readily established (Table 1).[12,13] Pyridinium dichromate was shown to be the oxidant of choice, compared with PCC and CrO_3.

Table 1



In theory, the oxidation of substrates having an allylsilane moiety could be plagued by competing annulation products, such as **6** (Eq. 2). However, this concern proved unfounded as the reaction of alcohol **5** with PDC affords only dienone **7**. Additional examples are summarized in Table 2.[14] This oxidative procedure is useful for preparative purposes as dienones **14** and **16** are routinely prepared from five grams of the appropriate alcohol.

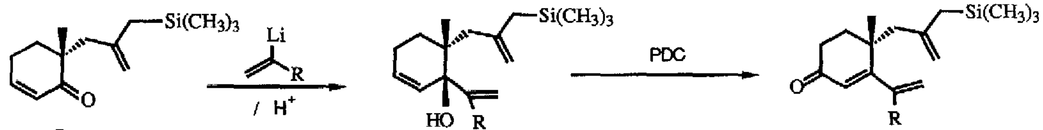
Equation 2



6 **5** **7**

The regiospecificity of these oxidations may be explained by examining conformers **iv** and **v** of the initially formed chromate ester (Eq. 3). In conformer **iv** the olefin within the ring is rigidly held in an orientation favorable for rearrangement, while in conformer **v** the exocyclic vinyl group is free to rotate away from the chromate ester, thus precluding rearrangement. Subsequent oxidation of the rearranged chromate ester **vi** proceeds irreversibly. This conjecture was easily proven by oxidation of dienol **17**, in which both vinyl groups are free to rotate (Eq.4). Treatment

Table 2



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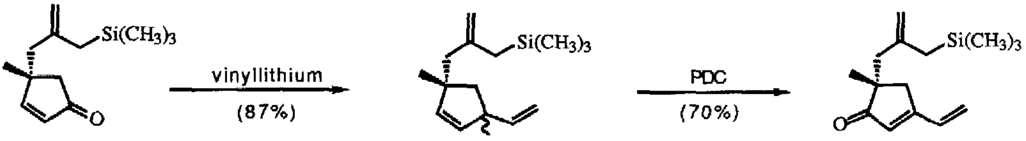
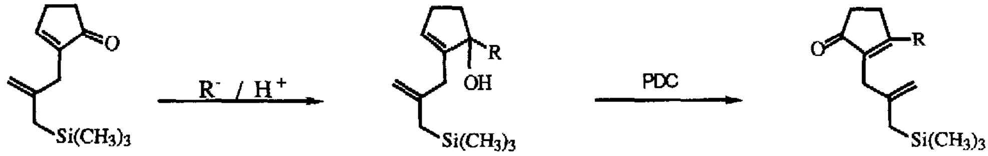
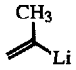
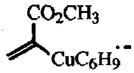
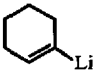
R =		
- H	97%	58% (**9**)
- CH(OEt)2	75%	60% (**10**)



11 **12**

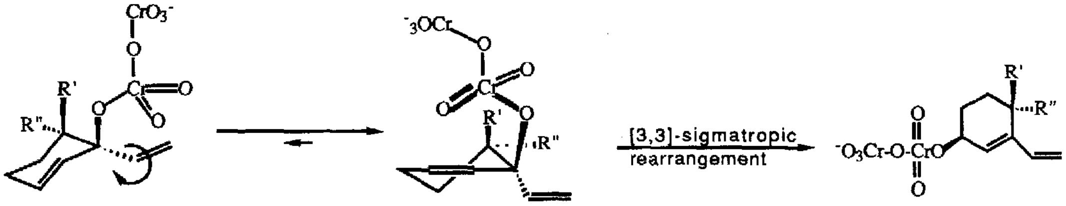


13

R⁻ =		
	91%	74% (**14**)
	62%	80% (**15**)
	78%	60% (**16**)

of **17** with PDC under standard conditions furnished an inseparable 2:1 mixture of dienone **18** and dienal **19** in 55% yield, showing that regiospecificity was indeed lost.

Equation 3



v **iv** **vi**

Equation 4

17 37% yield (**18**) 18% yield (**19**)

In conclusion, 1-vinyl-2-cycloalken-1-ols oxidize to form conjugated dienones in useful yields. Although the 1,3-oxidative rearrangment of dienols is quite general, this method is obviously limited by the availability of the requisite bis-allylic alcohol.

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References and Notes:

1. This work was presented in part at the 40th SERM at Atlanta, GA, in November, 1988; Abstract No. 545.
2. For a review of intramolecular additions of allylsilanes to dienones, see: Majetich,G.; Hull, K.; Lowery, D.; Ringold, C.; Defauw, J. "Intramolecular Additions of Allysilanes to Dienones." A chapter in *Selectivities in Lewis Acid-Promoted Reactions,* D. Reidel Co., Dordrecht, Holland (In press).
3. For a comprehensive review of allylsilane chemistry prior to 1981, see: Sakurai, H. Pure and Appl. Chem. **1982,** *54*, 1. For an updated survey of allylsilane chemistry, see: Majetich, G. "Allylsilanes in Organic Synthesis," in *Organic Synthesis, Theory and Applications*; Hudlicky, T. Ed., Jai Press, Inc., Greenwich, CT., **1988**, in press. Two reviews of allylsilane chemistry have recently appeared, see: Schinzer, D. Synthesis, **1988**, 263 and Hosomi, A. Acc. Chem. Res., **1988**, *21*, 200. A review of all aspects of allylsilane chemistry by I. Fleming and J. Dunogues is in press [Organic Reactions, *38*, Chapter 2].
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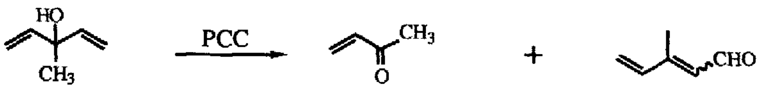
5. For the addition of [α-(alkoxycarbonyl)vinyl]cuprates to more reactive ketones, see: Marino, J.P.; Floyd, D.M. Tetrahedron Lett. **1975**, 3897.
6. Piers, E.; Chong, J. M. J. Org. Chem. **1983**, *48*, 1774.
7. Banfi, L.; Bernardi, A.; Colombo, L.; Gennari, C.; Scolastico, C. J. Org. Chem. **1984**, *49*, 3423.
8. Dauben, W. G.; Michno, D. M. J. Org. Chem. **1977**, *42*, 682.
9. For other examples of oxidative rearrangements using PCC, see: a) Wada, E.; Okawara, M.; Nakai, T. J. Org. Chem. **1979**, *44*, 2952. b) Corey, E. J.; Suggs, J.W. Tetrahedron Lett. **1975**, 2647. c) Babler, J.H.; Coghlin, M.J. Synth. Commun. **1976**, *6*, 469. For examples of oxidative rearrangements using PDC, see: d) Liotta, D.; Brown, D.; Hoekstra, W.; Monahan, R., III Tetrahedron Lett. **1987**, *28*, 1069. See, also: e) Corey, E.J.; Schmidt, G. Tetrahedron Lett. **1979**, 399. f) Corey, E.J.; Schmidt, G. Ibid. **1980**, 731. g) Sundararaman, P.; Herz, W. J. Org. Chem. **1977**, *42*, 813. h) Paquette, L.A.; Crouse, G.D.; Sharma, A.K. J. Am. Chem. Soc. **1982**, *104*, 4411.
10. In 1976 the following reaction was discovered by Babler and Coghlan; however, yields were not reported.[9c]



11. For a new preparation of dienones, see: Trost, B.M.; Schmidt, T. J. Am. Chem. Soc. **1988**, *110*, 2301.
12. a) All structures drawn here represent racemates, only one enantiomer being drawn. b) The spectroscopic data obtained for all new compounds were fully consistent with the assigned structures. c) Reaction conditions have not been optimized. d) All yields are isolated yields.
13. A typical procedure consists of using 1.5–2.0 equivalents of oxidant (PDC) and 500 mg of carbinol in dry CH_2Cl_2, followed by stirring at at room temperature for 8 hours and standard workup procedure.[9e]
14. The cyclizations of dienones **10**, **12**, **14**, **15** and **16** will be the subject of future reports.

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