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A 1,5-DIENE SYNTHESIS VIA TITANIUM AND ALUMINUM MEDIATED REACTIONS

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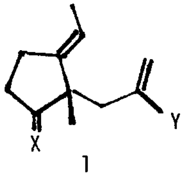
Abstract: (1) 1,5-Dienes are readily prepared by titanium mediated methylenation of allyl esters, Claisen rearrangement followed by a second methylene transfer reaction. (2) The same 1,5-diene may be approached in "one pot" combining an allyl acetate and 3 equivalents biscyclopentadienyl-titanium-μ-chloro-μ-methylidene-bismethyl aluminum.

In our ongoing investigation of boron annulation we had need of a 1,5-diene substrate of the general form:



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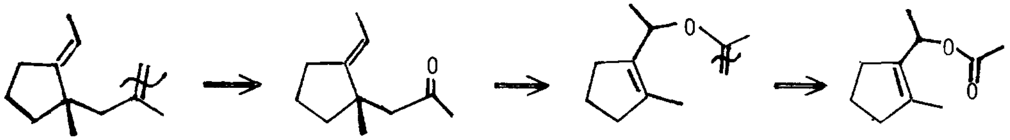
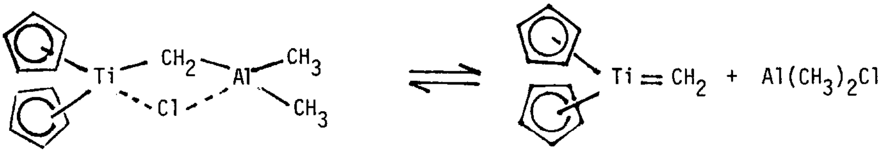
a) X = H,H; Y = alkyl b) X = O; Y= alkyl
c)X = OCH_2CH_2O; Y= alkyl d)X = SCH_2CH_2S;
Y = alkyl

Antithetically viewing the synthesis of substrate 1a suggested the use of γ,δ-eneone, 2, which would arise from thermolysis of appropriate allyl vinyl ethers, 3[3], or analogous Claisen rearrangement technique. Further, the retrosynthetic disjunctures of methylene groups in



1 2 3 5

structures 1 and 3 strongly alluded to recent developments in olefin synthesis utilizing direct methylenation of esters, ketones, lactones and aldehydes with the Wittig-like reagent biscyclopentadienyl titanium-μ-chloro-μ-methylidene bismethyl aluminum, 4 (Tebbe reagent).[4,5,6]



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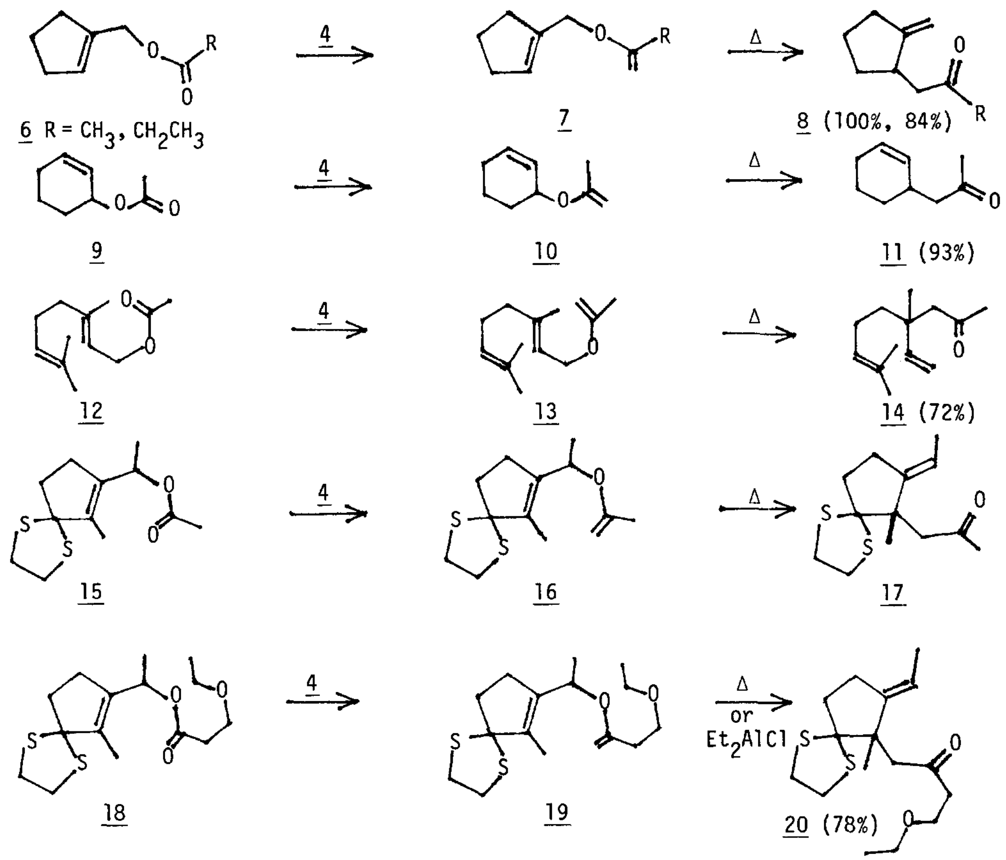
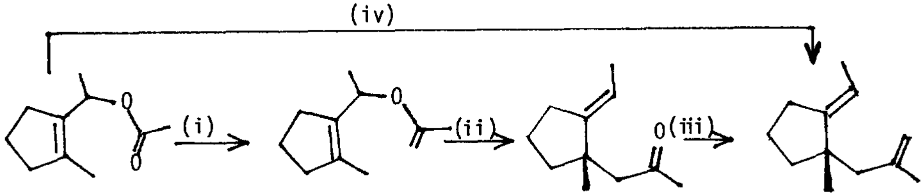
In practice we found that the Evans-Tebbe process was indeed a useful vehicle for conversion of allyl acetate 5 to allyl vinyl ether 3. Using the same experimental procedure described by Evans, the requisite allylic acetate, 5, as well as other model systems were converted to Claisen rearrangement substrates (See Scheme I).

Scheme I



Proceeding in the direction of diene 1, allyl vinyl ether 3 was thermalized in a Lindeburg oven (220°-320°C) using pentane as the solvent vehicle under argon. The condensed product (-78°) was chromatographed on silica gel to give γ,δ-eneone 2, in ~80% yield. This eneone, 2, was subsequently transformed to diene, 1, by a second use of 4. As would be expected, the model systems of Scheme 1 gave 1,5-dienes by this three step procedure. The tandem use of the Tebbe-Evans reaction with intermittent Claisen rearrangement gave rise to the potentiality of a "one-pot" approach to 1a wherein the incipient Lewis acid (presumably $Al(CH_3)_2Cl$) might possibly catalyze the desired [3,3] sigmatropic shift.[8,10] Only recently precedented,[7] this Lewis acid catalyzed rearrangement was in fact the case (Scheme II). The experimental details of a "one pot" conversion of allyl esters to their respective 1,5-dienes vary only slightly from Evans' procedure in that 3 equivalents of 4 were used rather than 1.1 eq and 20 µl pyridine per mmole of substrate was employed rather than the prescribed 10 µl. In addition, the reaction is allowed to stir for 12 hours at room temperature rather than the described 1.5 hours.

Scheme II



5a 3a 2a 1a

(i) 1.1 eq 4 for 1.5 hr (26°), 85%, (ii) 220°-320°, pentane, Ar, 50-80%,
(iii) 1.1 eq 4 for 1.5 hr (26°), 90%, (iv) 3 eq 4 for 12 hr (28°), 75%.

This methodology was extended through the series 6 → 18[11,12] of Scheme I. However, when dithialane allyl acetate 15 was reacted with 3 eq of 4 (12 hr at 25°) a mixture of 16 and 17 was apparent, suggesting a possible Lewis acid-Lewis base competition between sulfur and oxygen for the alleged dimethyl aluminum chloride, thus slowing the rearrangement process.[13] Continued investigations in this regard are underway.

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REFERENCES

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2) Author to whom all inquires should be addressed.
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8) The rationale of the Claisen transition state is as described by G. B. Bennett, Synthesis, 589 (1977); E to Z olefin configuration in 1a is 98:2.

9) Dithialane allyl vinyl ether 16 does not undergo Lewis acid catalyzed Claisen rearrangement with $AlCl_3$ (ϕH, 25°), while its analog 19 does undergo the desired [3.3] sigmatropic rearrangement in the presence of 2 equivalents of Et_2AlCl and 2.2 equivalents $P\phi_3$.[7]

10) Indicated compounds show satisfactory ^{1}H and ^{13}C NMR, IR, and mass spectra.

11) All compounds of Scheme I were converted to a 1,5 diene by the three step or one step process, allylacetate was also done but gave lower yields due to volatility.

12) (a) In the sequential preparation of 1,5-dienes from the model substrates of Scheme I, the crude allylic vinyl ethers are contaminated with Claisen rearrangement ketonic products when two equivalents of 4 are used. (b) Aluminum chloride assisted Claisen rearrangements of 3 failed to enhance yields of the desired products, while Et_2AlCl does effect conversion of 3 to 2 in an independent Lewis acid catalyzed Claisen rearrangement.

13) $AlCl_3$ had little effect on the Claisen rearrangement for the one-pot synthesis of 1a.

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