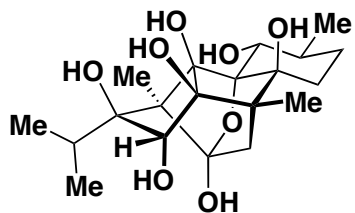


A. Bélanger; D. Berney; H. Borschber; R. Brousseau; A. Doutheau; R. Durand; H. Katayama; R. Lapalme; D. Leturc; C. Liao; F. MacLachlan; J. Maffrand; F. Marazza; R. Martino; C. Moreau; L. Saint-Laurent; R. Saintonge; P. Soucy; L. Ruest; P. Deslongchamps *Can. J. Chem.* **1979**, *57*, 3348.



Pierre Deslongchamps



1: ryanodol

-Pyrrolecarboxylate ester the active insecticidal component in the roots and stems of *Ryana speciosa*; binds nearly irreversibly to sarcoplasmic reticulum vesicles; binding studies identified calcium release channels now known as Ryanodine receptors

-Originally reported in 1948 by collaborators from Merck and the Department of Entomology at Rutgers University

-In 1967, Wiesner and co-workers elucidated the full structure **2** of natural ryanodine

-The X-ray structure of the p-bromobenzyl ether **3** of ryanodol was reported in 1972

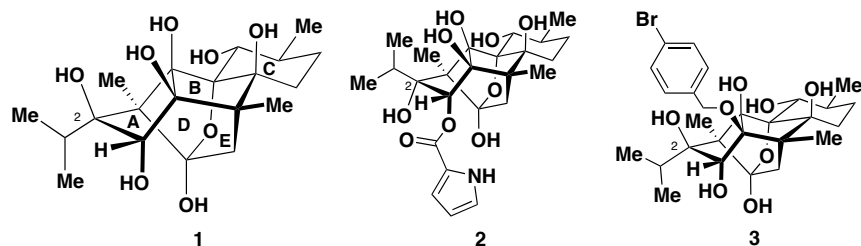
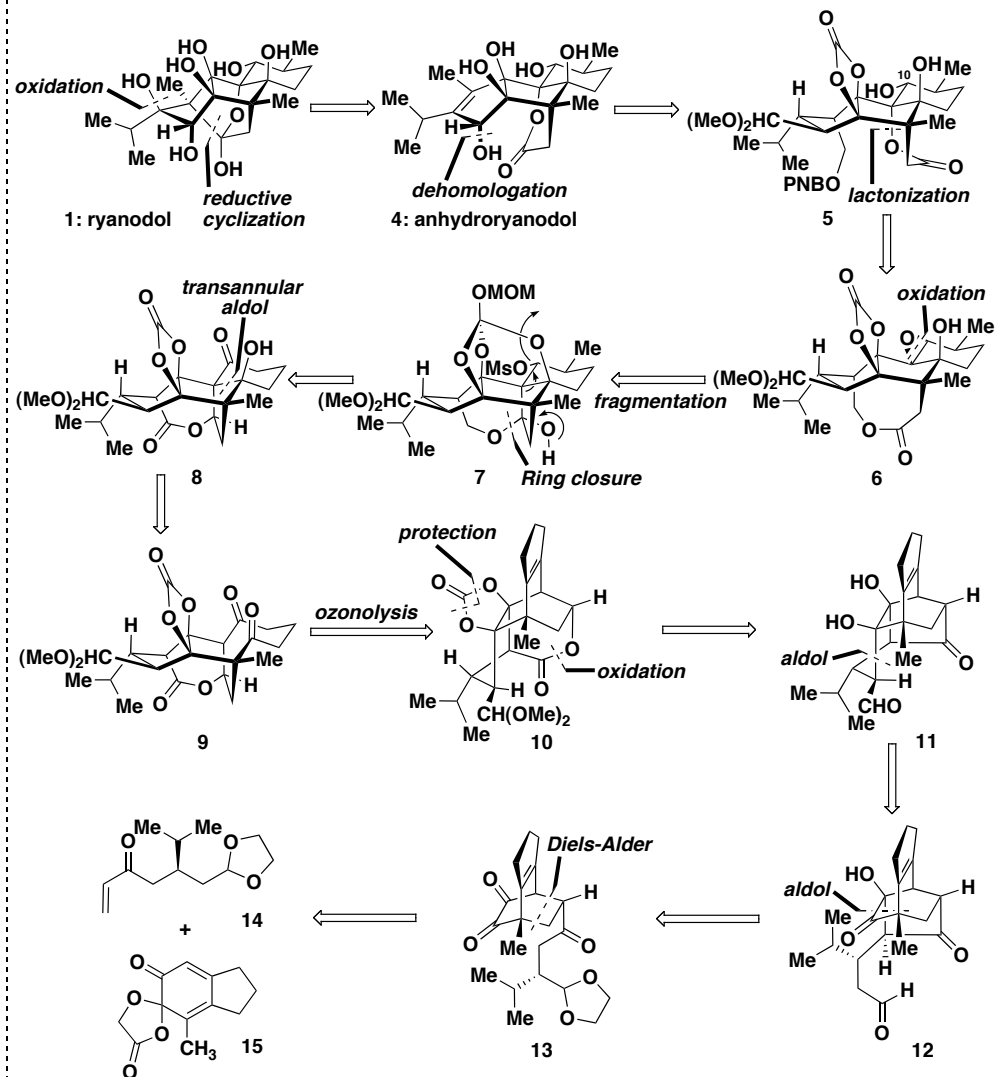
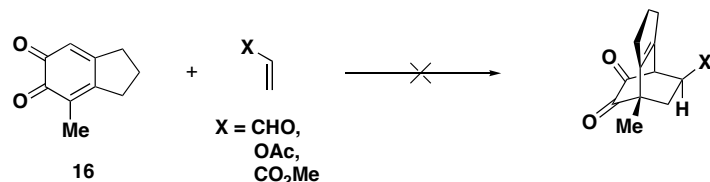


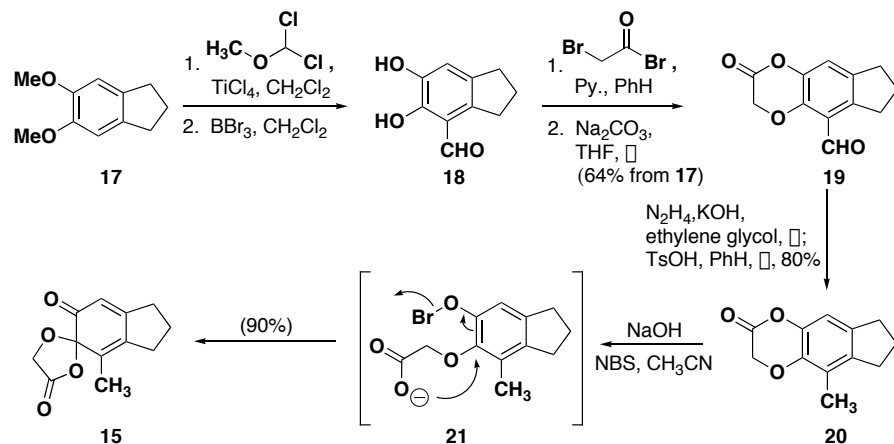
Figure 1. Ryanodol (1), Wiesner's proposed ryanodine (2) and a ryanodol derivative (3) assigned by X-ray crystallography.



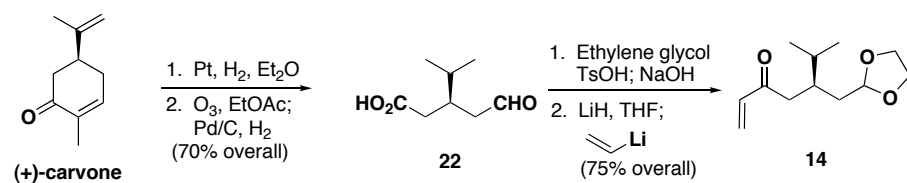
Scheme 1. Retrosynthetic analysis of ryanodol (1).



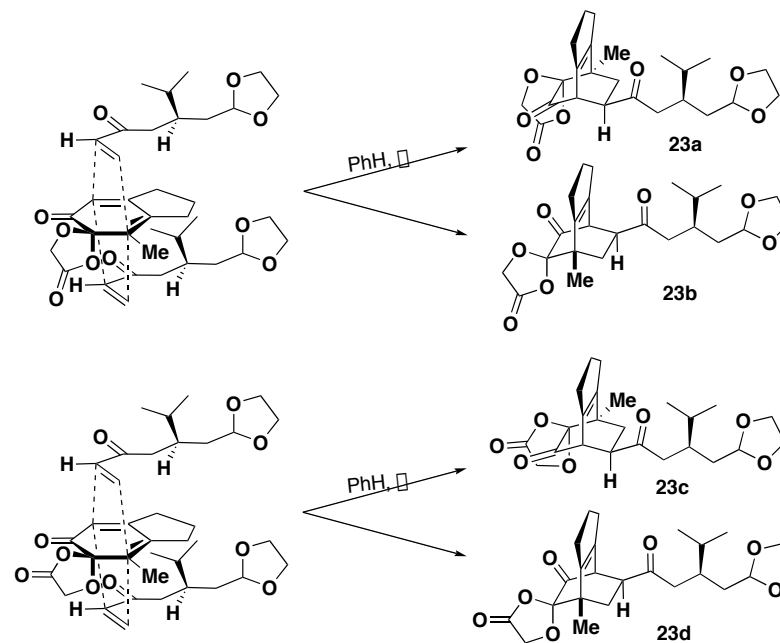
Scheme 2. Initial attempts at *o*-quinone Diels-Alder reactions.



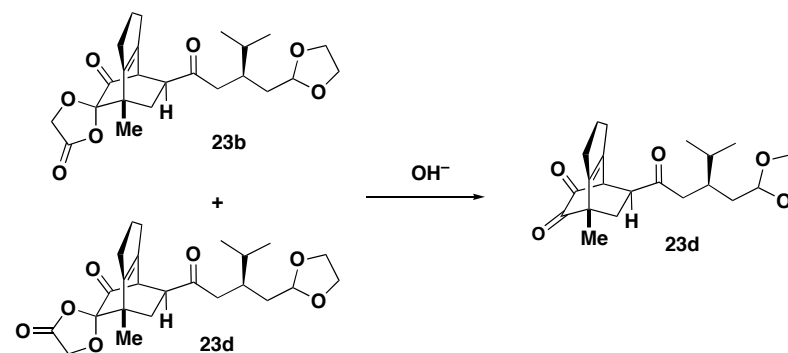
Scheme 3. Synthesis of an *o*-quinone surrogate diene.



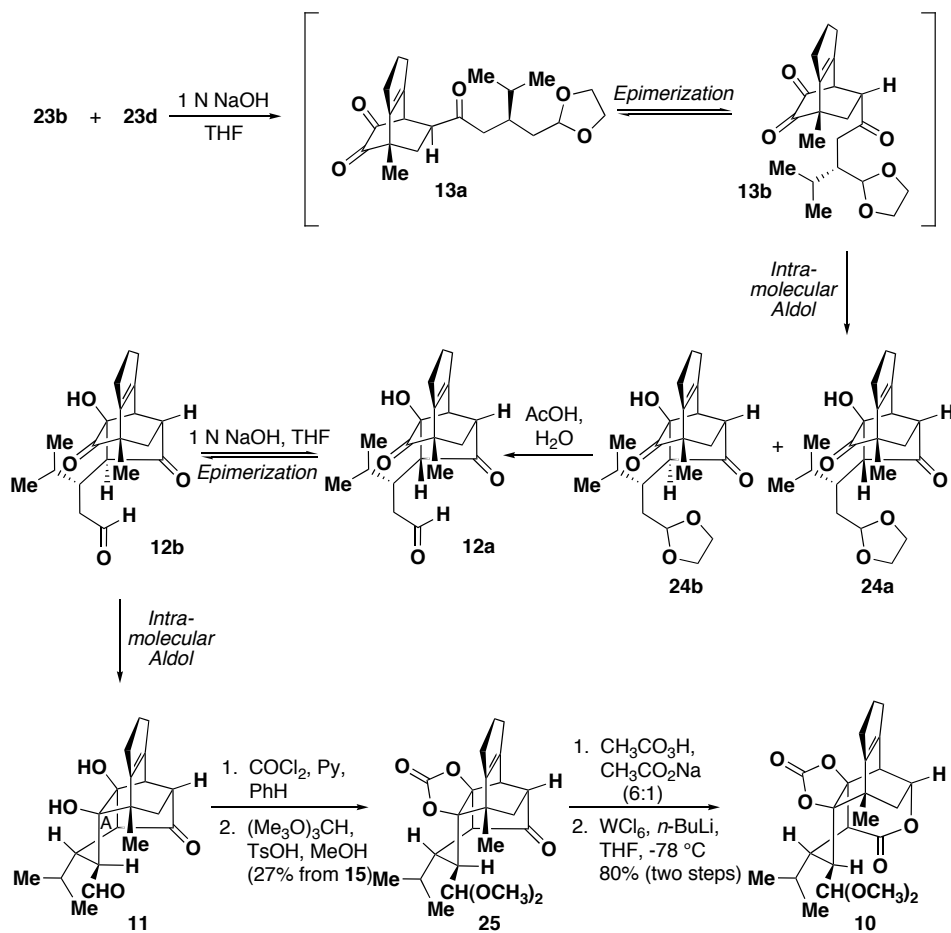
Scheme 4. Synthesis of the optically active dienophile.



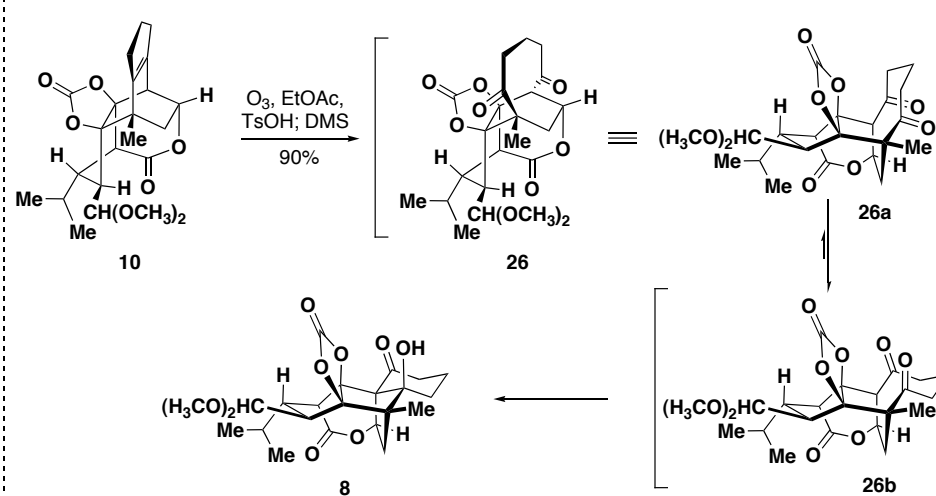
Scheme 5. The Diels-Alder reaction and products formed.



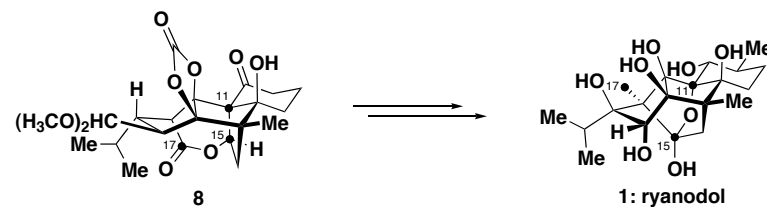
Scheme 6. Isomer equivalency.



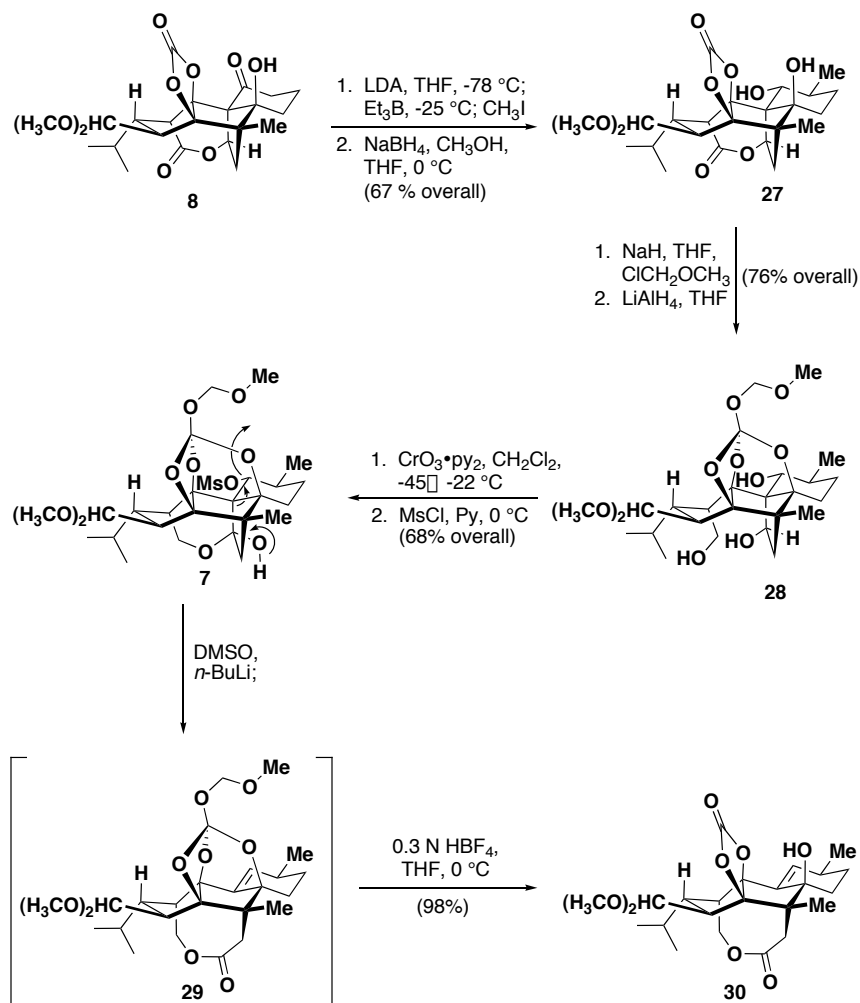
Scheme 7. Construction of the A ring of ryanodol (1).



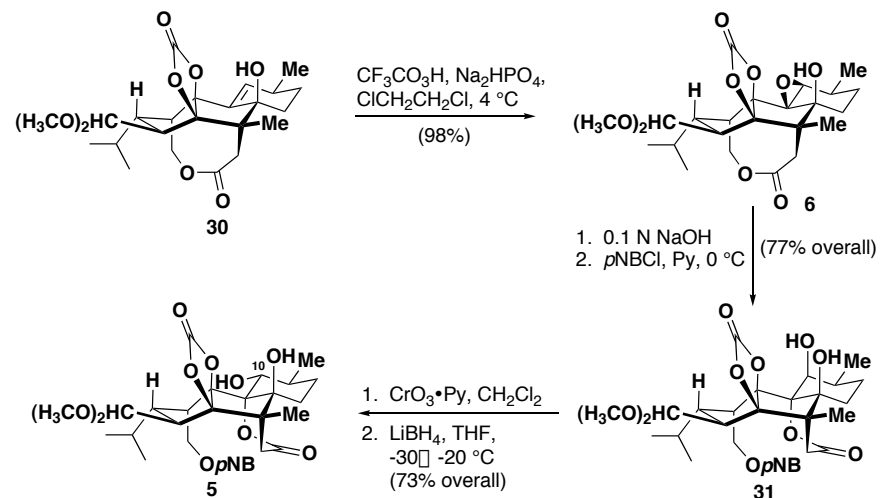
Scheme 8. The ozonolysis cascade to establish the A, B, and C rings of ryanodol (1).



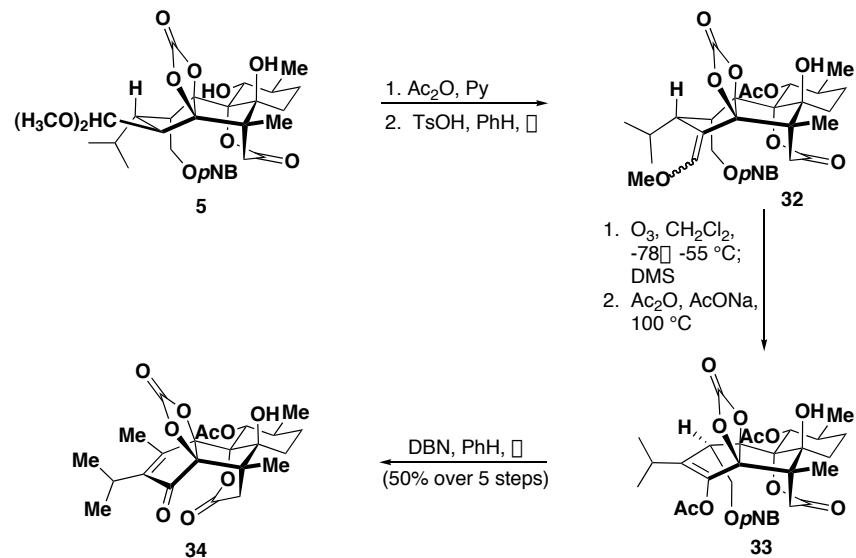
Scheme 9. Desired oxidation state changes between intermediate 8 and ryanodol (1).



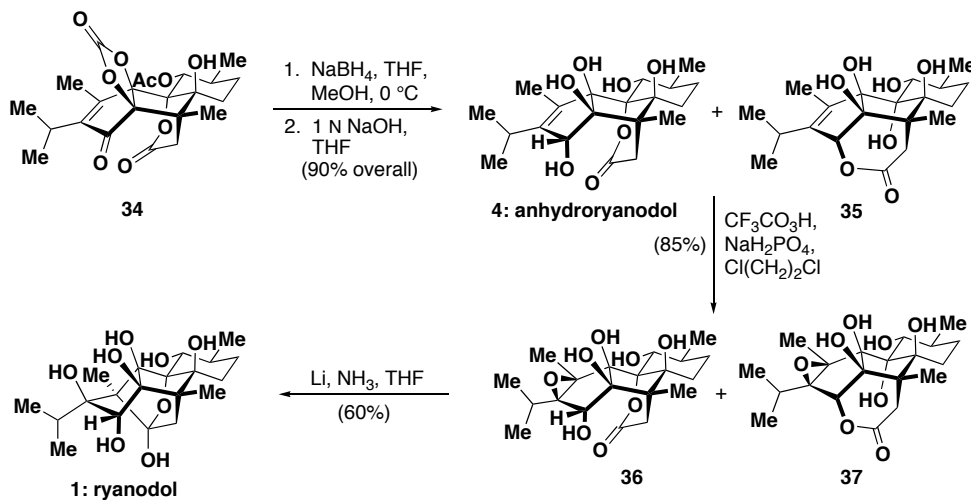
Scheme 10. Synthesis of intermediate 30.



Scheme 11. Synthesis of advanced intermediate 5.

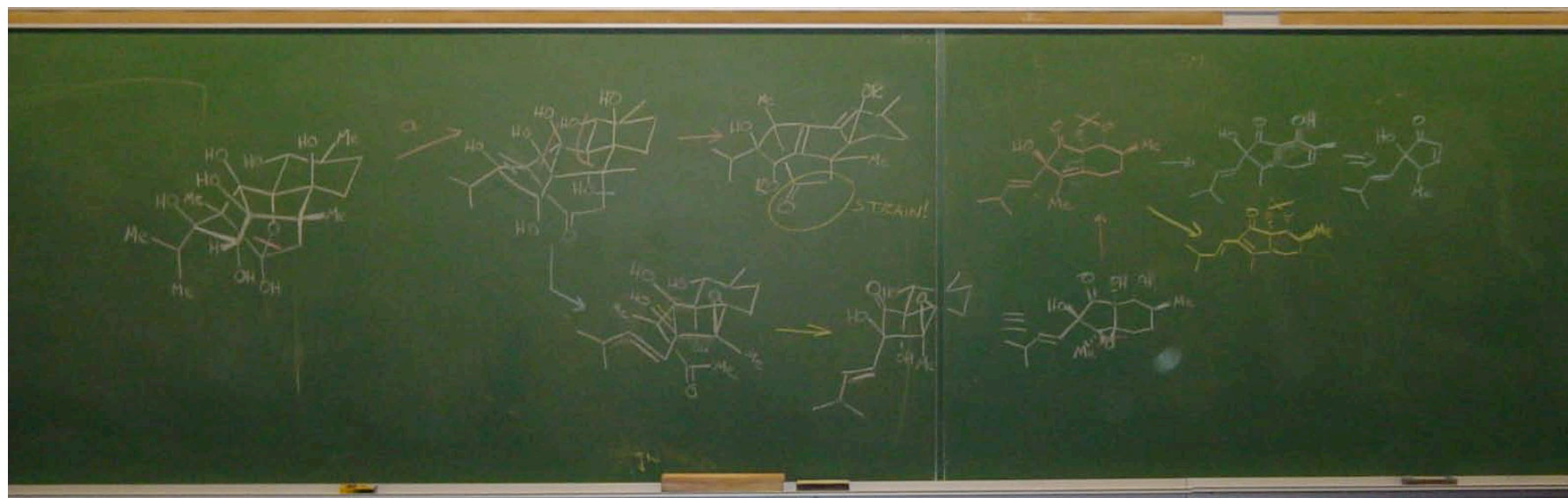
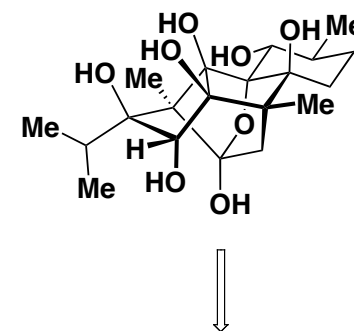


Scheme 12. Formal reduction of C17 to achieve intermediate 34.



Scheme 13. Endgame construction of anhydroryanodol (4) and ryanodol (1).

Your own disconnections:



Scheme 14. Impromptu group disconnections of ryanodol (1).