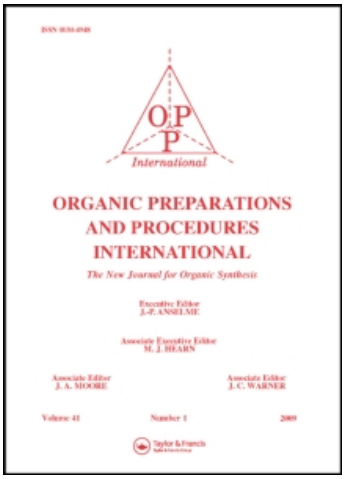

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SYNTHESIS OF SATURATED γ-LACTONES. A REVIEW

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SYNTHESIS OF SATURATED γ-LACTONES. A REVIEW

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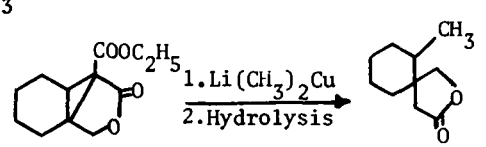
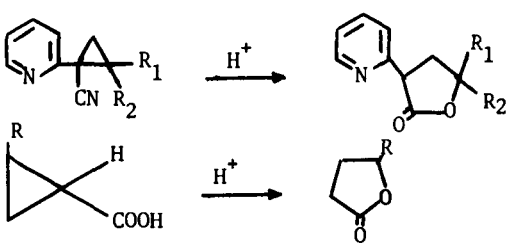
γ-Lactones are ubiquitous natural products. They have commanded continuous attention owing to their economic values and their being convenient models for many new synthetic approaches.

The aim of this review is to bring together various synthetic routes for the preparation of saturated γ-lactones in a flow chart format.

1. From Cyclopropanes[1-3]

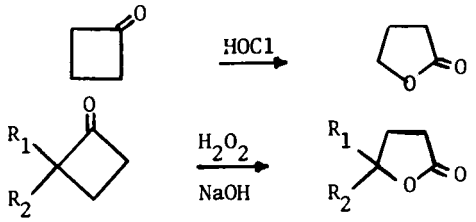


Lithium dimethyl copper opening of cyclopropyl lactone followed by hydrolysis and decarboxylation gives spiro-γ-lactone.

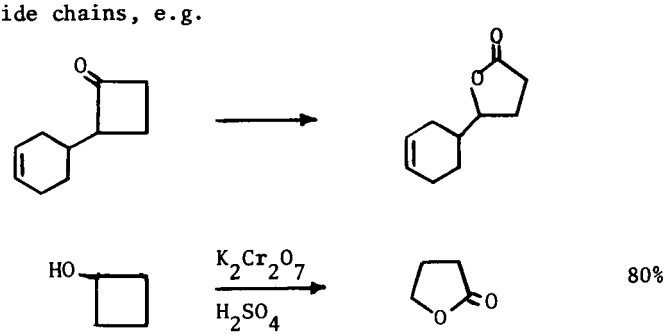


Cyclopropane carboxylic acids undergo acid-catalyzed rearrangement to γ-butyrolactones.

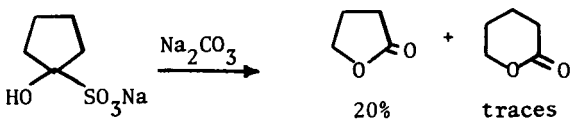
2. From Cyclobutanes[4-6]



Treatment of cyclobutanone with basic hydrogen peroxide in methanol solution at room temperature allows smooth conversion to γ-butyrolactone. This method is highly stereoselective and allows the presence of double bonds in the side chains, e.g.

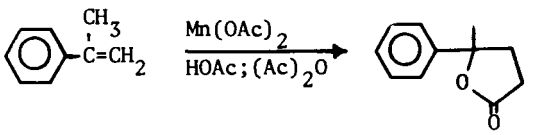


3. From Cyclopentanone[7]

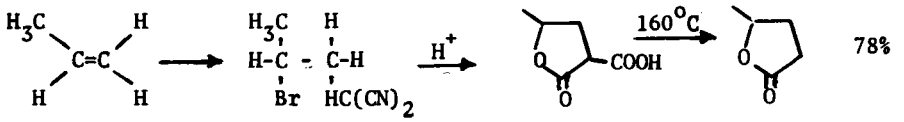


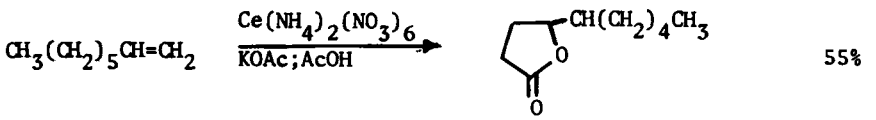
Anodic oxidation of sodium bisulfite addition product of cyclopentanone affords a mixture of γ- and δ-lactones.

4. From Olefins and Epoxides[8-13]

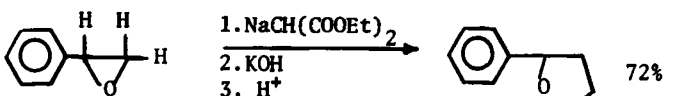


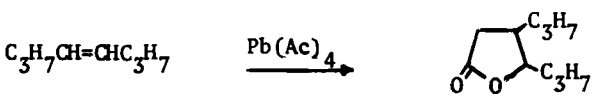
Acetic anhydride has dramatic effect on both, rate and yield of the reaction. Thus 72% yield is obtained within 90 minutes in the presence of acetic anhydride, in its absence and during 24 hours, the yield drops to 25%.



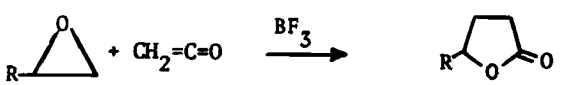


The reaction of ceric salts and carboxylates with aliphatic and aromatic olefins has broad synthetic utility for the facile preparation of γ-lactones.



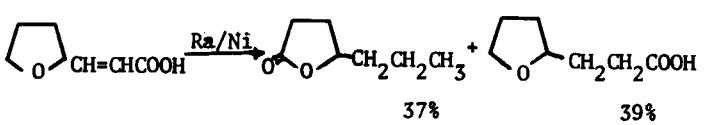


The γ-lactone is formed as a by-product in the oxidation reaction of the olefin.



Addition reaction of 1,2-epoxides with ketene, in presence of BF_3 as catalyst affords γ-substituted-γ-butyrolactones in 10% yields.

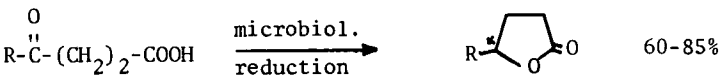
5. From Unsaturated Acids[14]



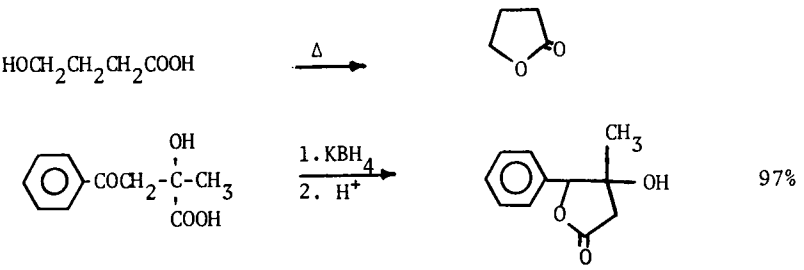
This synthesis furnishes a mixture of alkyl-γ-lactone and furan-

propionic acid.

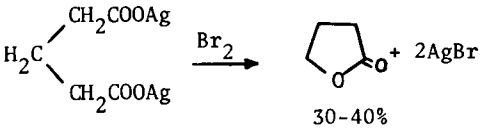
6. From Hydroxy Acids[15,16]



The product is optically active.

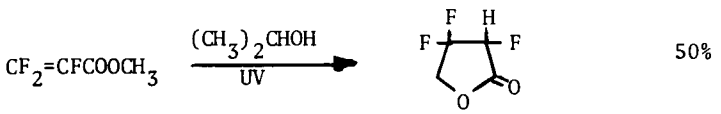


7. From Diacids[17]

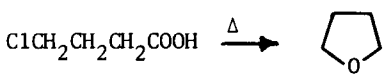


This is a modified Hunsdiecker decarboxylation.

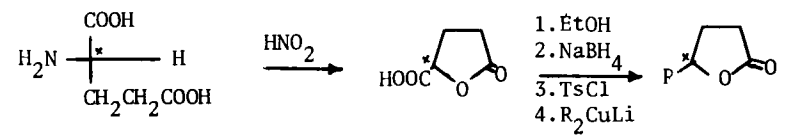
8. From Halo Acids[18]



Photochemically initiated reaction of 2-propanol with methyl-trifluoroacrylate in liquid phase affords fluorinated γ-lactones in good yields.

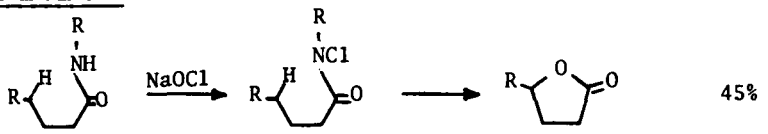


9. From Amino Acids[19]

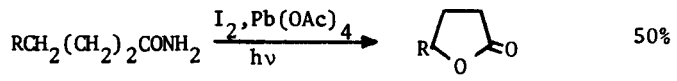


This route appears to be an attractive one because the starting materials are available and the product is optically active.

10. From Amides[20,21]

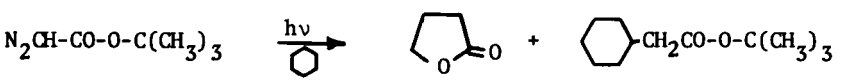


γ-Lactones are formed by thermolytic homolysis of N-chloro amides.

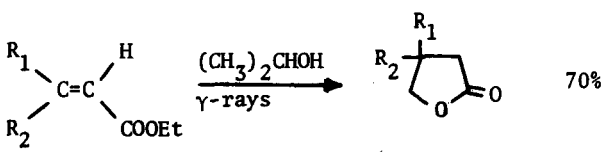


Lactonization is most conveniently effected by photolysis of the amide in the presence of excess of iodinating agent such as iodine with t-butylhypochlorite or lead tetraacetate.

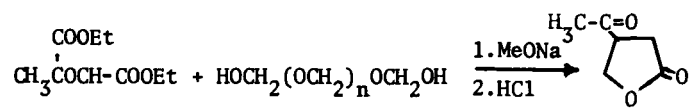
11. From Esters[22-24]



By photolysis of t-butyl ester of diazoacetic acid.

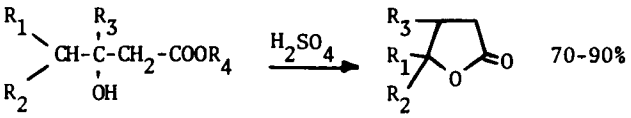


By irradiation-induced addition of alcohol to α,β-unsaturated ester.



By base-catalyzed aldol condensation of substituted malonic and acetoacetic ester with paraformaldehyde.

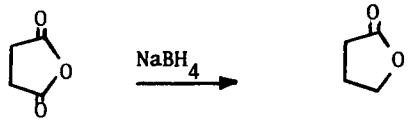
12. From Hydroxy Esters[25]



70-90%

The yield is high when there is at least one secondary or tertiary alkyl group on carbon 3 (R_1 or R_2). The method is especially suitable for the synthesis of γ,γ-disubstituted γ-lactones.

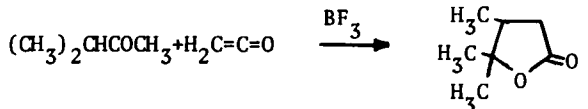
13. From Cyclic Anhydrides[26]



90%

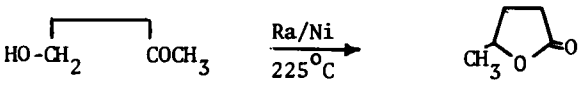
Cyclic anhydrides may also be reduced to γ-lactones with sodium or sodium amalgam in alcohol; sodium borohydride however, is an exceptionally mild reducing reagent.

14. From Ketones and γ-Hydroxyketones[27,28]



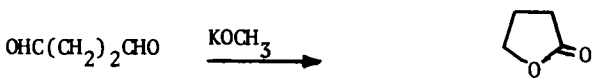
41%

By reaction of ketones with ketenes in presence of boron trifluoride.

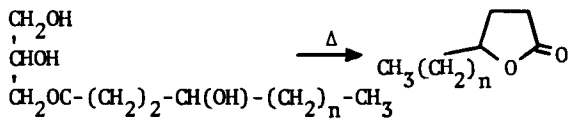


86%

15. From Dialdehydes[29]

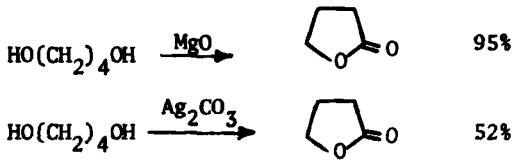


16. From Glycerides[30]



By cyclization of γ-hydroxy acid moiety of glycerides.

17. From 1,4-Diols[31,32]

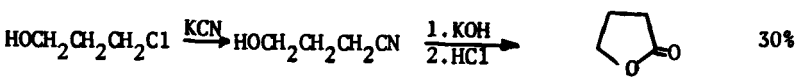


Silver carbonate in Celite oxidizes primary 1,4-diols into γ-lactones in good yields.

18. From β-Allenic Alcohols[33]

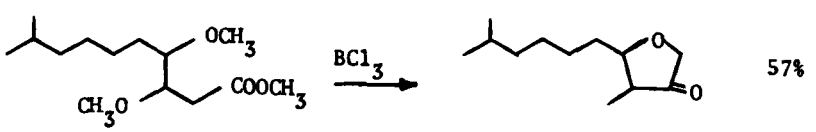
This is a selective oxidation method of β-allenic alcohols.

19. From 1,3-Chlorohydrins[34]

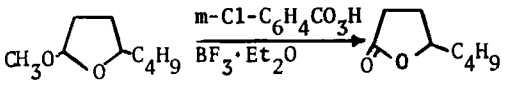


20. From Ethers[35,36]

Tetrahydrofuran is oxidized smoothly to γ-butyrolactone in quantitative yield.

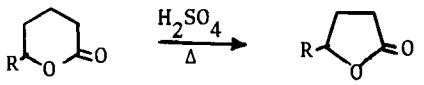


21. From Lactols[37]

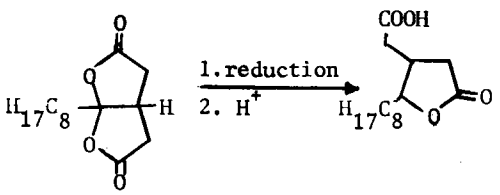


Treatment of protected lactol with m-chloroperbenzoic acid in methylene chloride containing a catalytic amount of boron trifluoride etherate forms γ-lactones in good yields.

22. From δ-Lactones[38]

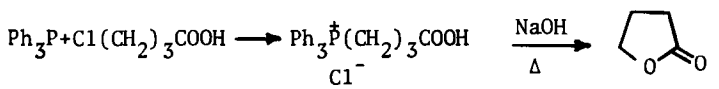


23. From bis-Lactones[39]



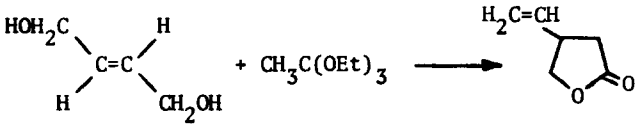
Treatment of bis-lactone with $NaBH_4$ in aqueous potassium hydroxide solution leads after acidication to pure trans-tetrahydro-2-(n-octyl)-5-oxo-3-furanacetic acid in 91% yield.

24. By Wittig-type Synthesis[40]



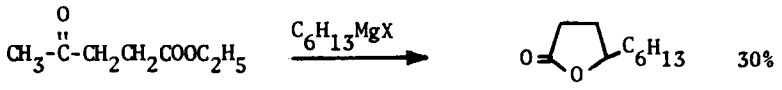
γ-Butyrolactone is formed through an intermediate phosphonium salt.

25. By Claisen Rearrangement[41]



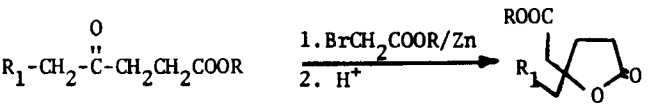
89%

26. By Grignard Synthesis[42,43]

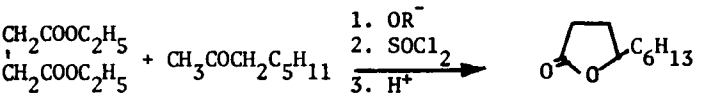


30%

27. By Reformatzky Synthesis[44]

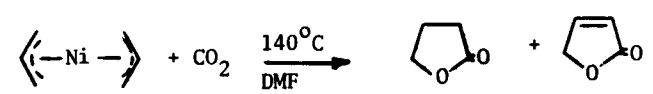


28. By Stobbe Condensation[45,46]



81%

29. From Allyl Nickel Complexes[47]



32%

There is remarkable solvent effect on CO_2 absorption; 90% in DMF; 1% in C_6H_6.

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Note: A review entitled "The synthesis of lactones and lactams" by J. F. Wolfe and M. A. Ogliaruso, in The Chemistry of Functional Groups, Supplement B, The Chemistry of Acid Derivatives, Part 2, 1064, S. Patai, Editor, John Wiley, 1979, was published when this review was in press. Some of the synthetic methods mentioned in the present review were described in detail in the above mentioned review.

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