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CONVERSION OF OLEFINS INTO γ-BUTYROLACTONES

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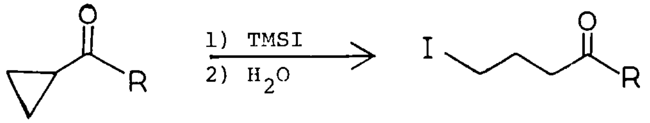
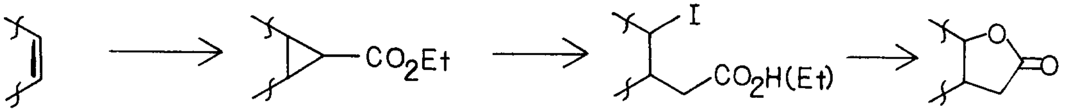
Summary: Cyclopropyl esters derived from olefins undergo ring opening with iodotrimethylsilane and, after base treatment, γ-butyrolactones are obtained.

In connection with a recent synthetic effort, a method for the conversion of a carbon-carbon double bond into a γ-butyrolactone was needed.[1] The recent work by Miller[2,3] on iodotrimethylsilane (TMSI) opening of cyclopropyl and cyclobutyl ketones (e.g., eq 1) suggested a very convenient approach to accomplish this goal in three steps (eq 2). A wide variety of olefins can be converted into cyclopropyl esters in high yields by the catalyzed addition of ethyl diazoacetate.[4,5] Opening of the cyclopropane ring with TMSI[6] and ring closure to the lactone by loss of HI and/or ethyl iodide would complete the overall conversion.[7,8]



(1)



(2)

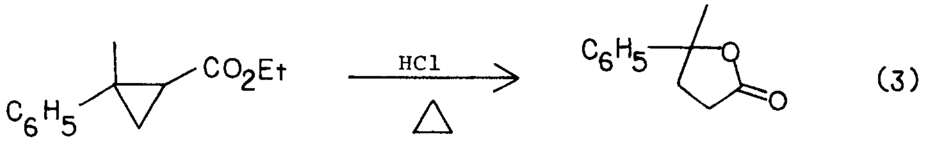
In order to test the crucial step, cyclopropanecarboxylic acid was allowed to react with excess TMSI in the presence of a catalytic amount of mercury.[2] Impure γ-iodobutyric acid was obtained. Zinc iodide[2] is also an effective catalyst although the reaction works well (98% yield) when no catalyst is used.

Ethyl cyclopropanecarboxylate reacts with excess TMSI in the presence of zinc iodide but the reaction does not go to completion. It is striking that omission of the "catalyst" allows complete consumption of starting material[9] and formation of γ-iodobutyric acid plus the ethyl ester in a 3:1 ratio. Unfortunately neither hydrogen iodide[10] nor chlorotrimethylsilane and sodium iodide[11] would induce the opening of ethyl cyclopropanecarboxylate.

Ring closure of the iodo compounds into lactones was straightforward. γ-Iodobutyric acid gave butyrolactone in 85% yield upon exposure to potassium carbonate in refluxing tetrahydrofuran (THF). The corresponding ethyl ester was unaffected by this treatment; however, successful conversion of the mixture of γ-iodobutyric acid and the ethyl ester into butyrolactone was accomplished with potassium carbonate and silver nitrate in refluxing THF.

This lactone synthesis was extended to other olefinic substrates (see Table I). For example, 1-hexene was converted into ethyl 2-butylcyclopropanecarboxylate using ethyl diazoacetate. Excess TMSI gave 3-iodomethylheptanoic acid in quantitative yield. Base-catalyzed ring closure yielded 3-butylbutyrolactone (89%).

This procedure did not work with aromatic olefins. Thus, both α-methylstyrene and indene were converted into the corresponding cyclopropyl esters but treatment with TMSI did not give readily identifiable products. Fortunately, cyclopropyl esters capable of giving stable carbonium ions upon protonation can yield butyrolactones directly upon reaction with acid when heated.[12] Application of this strategy to the cyclopropyl ester derived from α-methylstyrene gave an 80% yield of the corresponding lactone (eq 3). Furthermore, this hydrogen chloride-catalyzed lactone formation allows the reversal of the regiochemistry of the lactone product obtained from TMSI (e.g., eq 4).



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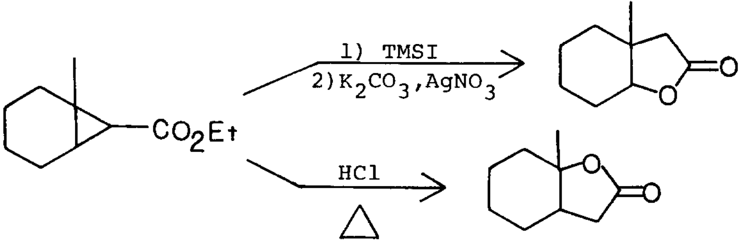

(4)

In conclusion, this method for the conversion of olefins into butyrolactones is a general one with predictable stereochemistry and regiochemistry. This should supplement the currently available alternatives.

REFERENCES AND NOTES

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1. Literature methods for this conversion are as follows: (a) Dichlorocarbene cycloaddition with olefins, dechlorination and Baeyer-Villiger oxidation: for example, see P. A. Grieco and K. Hiroi, Tetrahedron Lett., 3467 (1974). (b) Manganese (III) or cerium (IV) catalyzed addition of acetic acid to olefins: J. B. Bush, Jr. and H. Finkbeiner, J. Am. Chem. Soc., 90, 5903 (1968); E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., ibid., 90, 5905 (1968) E. I. Heiba and R. M. Dessau, ibid., 93, 995 (1971); M. Okano, Bull. Chem. Soc. Jap., 49, 1041 (1976). (c) Chloronitrone cycloaddition to olefins and hydrolysis: A. Ruttimann and D. Ginsburg, Helv. Chim. Acta, 58, 2237 (1975). (d) Malonate opening of epoxides and hydrolysis: M. S. Newman and C. A. Van der Werf, J. Am. Chem. Soc., 67, 233 (1945); J. A. Marshall and N. Cohen, J. Org. Chem., 30, 3475 (1965). (e) Carboxylate dianion opening of epoxides: P. L. Creger, J. Org. Chem., 37, 1907 (1972); T. Fujita, S. Watanabe and K. Suga, Aust. J. Chem., 27, 2205 (1974); S. Danishefsky, M.-Y. Tsai and T. Kitahara, J. Org. Chem., 42, 394 (1977). (f) Oxazoline anion opening of epoxides: A. I. Meyers, E. D. Mihelich and R. L. Nolen, J. Org. Chem., 39, 2783 (1974). (g) α-Trimethylsilylacetonitrile anion opening of epoxides: C. W. Bock, P. George, M. Trachtman and M. Zanger, J. Chem. Soc., Perkin II, 26 (1979). (h) Ketene acetals plus epoxides: J. W. Scheeren, F. J. M. Dahmen and C. G. Bakker, Tetrahedron Lett., 2925 (1979). (i) For a recent review on the synthesis of saturated γ-lactones, see R. Ikan, V. Weinstein and U. Ravid, Org. Prep. Proc. Int., 13, 59 (1981).
2. (a) R. D. Miller, D. R. McKean and D. Kaufmann, Tetrahedron Lett., 587 (1977). (b) R. D. Miller and D. R. McKean, ibid., 2305 (1979). (c) R. D. Miller and D. R. McKean, J. Org. Chem., 46, 2412 (1981) and references cited therein.
3. Pyridinium hydrochloride also opens cyclopropyl ketones to give γ-chloroketones: E. Giacomini, M. A. Loreto, L. Pellacani and P. A. Tardella, J. Org. Chem., 45, 519 (1980).
4. J. A. Berson and E. S. Hand, J. Am. Chem. Soc., 86, 1978 (1964); R. T. LaLonde and M. A. Tobias, ibid., 86, 4068 (1964); W. Kirmse and K.-H. Pook, Chem. Ber., 98, 4022 (1965); J. Warkenton, E. Singleton and J. F. Edgar, Can. J. Chem., 43, 3456 (1965); E. W. Warnhoff and V. Dave, ibid., 44, 621 (1966).
5. Other routes to cyclopropyl esters include addition of either diazoalkanes (e.g. see S. Siegel and C.G.Bergstrom, J.Am.Chem.Soc., 72, 3815 (1950)) or

sulfoxonium ylides (e.g. see C. Kaiser, B. M. Trost, J. Beeson and J. Weinstock, J. Org. Chem., 30, 3972 (1965)) to α,β-unsaturated esters.

6. Unfortunately, Miller reports that cyclopropyl esters are unreactive toward TMSI.[2c]
7. α-(Dimethylaminomethyl)-cyclopropyl esters rearrange in the presence of hot TMSI into α-methylene γ-lactones: T. Hiyama, H. Saimoto, K. Nishio, M. Shinoda, H. Yamamoto and H. Nozaki, Tetrahedron Lett., 2043 (1979).
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11. This combination often can be substituted for TMSI; G. A. Olah, S. C. Narang, B. G. B. Gupta and R. Malhotra, J. Org. Chem., 44, 1247 (1979).
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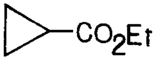
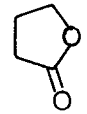
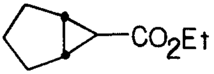
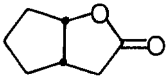
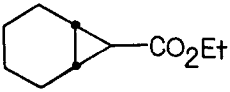
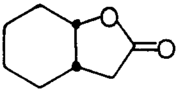
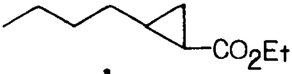
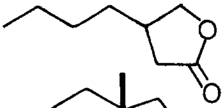
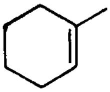
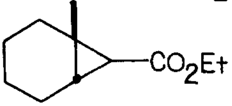
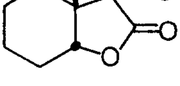
Table I. Conversion of Olefins into Butyrolactones

Olefin	Cyclopropyl ester (%Yield)[a]		% Yield of Iodo Compounds	Butyrolactone (%Yield)[a,]	
			89		(72)[c]
		(79)	96		(82)
		(73)	100		(86)
		(43)	100		(89)
		(83)	74		(89)[c]

[a] All yields refer to distilled products which are obtained stereochemically pure

[b] Obtained by TMSI opening (using 2-6 equiv. of TMSI for 2-4 days) of the cyclopropyl ester followed by ring closure with K_2CO_3 in refluxing THF for 1-4 days.

[c] $AgNO_3$ and K_2CO_3 for 1-5 days were used for ring closure.

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