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BIS(TRIMETHYLSILYL) SULPHATE CATALYZED γ-LACTONIZATION OF CYCLOPROPANECARBOXYLATES HAVING A CARBONYL SUBSTITUENT AT CYCLOPROPANE α-CARBON

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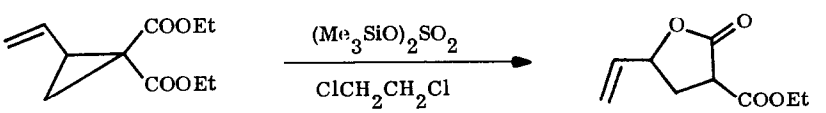
The oxa analogue of vinylcyclopropane rearrangement in the title system is carried out under mild conditions with the aid of the silicon Lewis acid catalyst.

Bis(trimethylsilyl) sulphate (BTS)[1-3] is characterized by high Lewis acidity and low nucleophilicity, although the synthetic application of this reagent has been limited so far only to silylation of active hydrogen compounds.[4,5] We have found that the appropriately activated cyclopropanecarboxylates are readily transformed into γ-butyrolactones by the catalysis of this reagent.

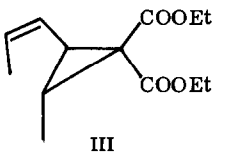
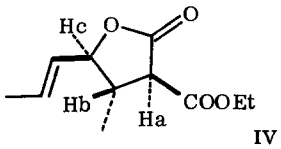
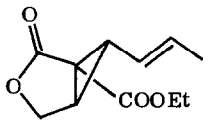
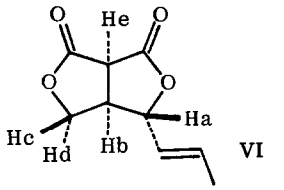
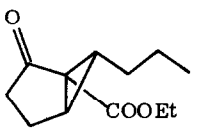
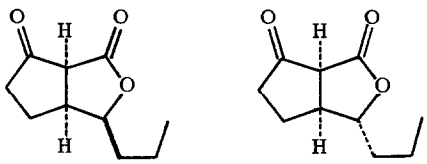
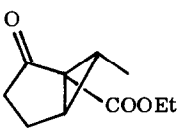
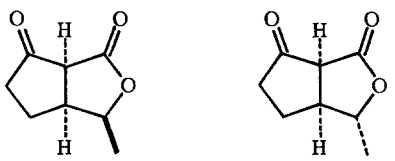
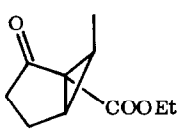
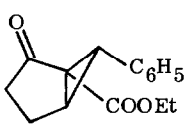
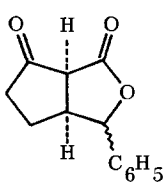
When a 1,2-dichloroethane (2 ml) solution of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (I) (82 mg, 0.4 mmol) was heated to reflux in the presence of BTS (0.20 g, 0.8 mmol) for 1 h, the γ-butyrolactone II[6,7] was produced in 98% yield after TLC purification. Other possible product such as ethyl 3-cyclopentene-1,1-dicarboxylate or a seven-membered ring lactone was not detected at all. The BTS catalyst is markedly expedient for this transformation as following catalysts gave inferior yields of II: H_2SO_4, 61%;[8a] $Me_3SiOSO_2CF_3$, 25%;[8b] $Me_3SiOClO_3$ (prepared from $AgClO_4$ and Me_3SiCl), 39% in benzene,[8c] 30% in dichloromethane;[8d] Me_3SiI, 0%;[8e] $BF_3{\cdot}OEt_2$, complex mixture of products; Et_2AlBF_4 (prepared from Et_2AlCl and $AgBF_4$), 0%;[8f] $TiCl_4$, no reaction.



I II

Such cyclopropanecarboxylates as ethyl chrysanthemate, trans-2-vinyl-1-(1-oxo-3-phenylpropyl)-cyclopropane and ethyl trans-2-phenylcyclopropanecarboxylate failed to be transformed into the corresponding γ-lactones. Obviously the gem-dicarbonyl substitution on a cyclopropane carbon is required for the lactonization of this kind. It is worthy, however, to point out that the catalyzed oxa-vinylcyclopropane rearrangement takes place under mild conditions (40-80°) compared with the purely thermal reaction which generally is carried out at over 280°.[9,10]

Table 1 Transformation of α-Carbonyl Substituted Cyclopropanecarboxylates into γ-Butyrolactones with BTS Catalyst[a]

Substrate	Temp (°)	Yield (%)	Product(s) (ratio)
 III	40[b]	63 (98)[c]	 IV
 V	80	39[d]	 VI
 VII	80	79[e]	 VIIIa (82:18) VIIIb
 IX	80	71	 Xa (65:35) Xb
 XI	80	28[d]	Xa (23:77) Xb
	80	28[f]	

a) Typically 1 mol of the substrate was heated in the presence of 2 mol of BTS in 1,2-dichloroethane. b) The reaction was carried out in dichloromethane. c) Based on the consumed starting material. d) Other product was polymeric material ($R_f \sim 0$ on TLC) only. e) BTS (1 mol) was employed. f) A by-product, 3-benzyl-2-ethoxycarbonyl-2-cyclopentenone (24%), was formed.

Other cyclopropanecarboxylates reacting expectedly are summarized in Table 1. Diethyl trans-2-methyl-3-(cis-1-propenyl)cyclopropane-1,1-dicarboxylate (III) was converted into the lactone IV[7,11] of the depicted stereochemistry. Although the trans arrangement of the methyl and 1-propenyl appendages in III is retained in the product IV, the isomerization of the cis C=C bond to trans is remarkable.[12] Retention of the stereochemistry at the cyclopropane carbon is observed again in the reaction of V to the lactone VI[7] which was proved to have the 1-propenyl substituent at the exo position.[13]

In contrast, opposite stereochemistry prevails in the reaction of substrates having no cation-stabilizing substituent like 1-propenyl group. The dihydro derivative VII was transformed into an 82:18 mixture of the endo-propyl lactone VIIIa and the exo-propyl one VIIIb.[7,14] Similarly, IX gave a 65:35 mixture of Xa and Xb.[7] The somewhat sluggish reaction of the endo methyl isomer XI gave the exo methyl lactone Xb[7] predominantly. Thus, the γ-lactonization of VII, IX and XI proceeds mostly with the inversion of the configuration at the migrating cyclopropane carbon. These results are comparable with the stereochemical data of thermal vinylcyclopropane⟶cyclopentene rearrangement (ca 300°) wherein approximately 70% inversion at the migrating terminus is recorded.[15,16]

Study aiming at the application of the BTS catalysis to synthetic reactions is now in progress.

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2. N. Duffaut, R. Calas, and J. Dunogues, Bull. Soc. Chim. Fr., 1963, 512
3. M. Schmidt and H. Schmidbaur, Chem. Ber., 94, 2446 (1961)
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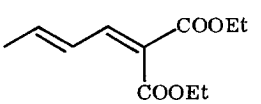
6. Bp 125-130° (bath temp)/0.06 Torr; MS: m/e 184 (M^+); IR (neat): 1780, 1740, 1162 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.34 (t, 3H), 2.0-2.9 (m, 2H), 3.48 (dd, J = 9.6, 5.7 Hz, 1H), 4.24 (q, 2H), 4.7-5.2 (m, 1H), 5.2-5.6 (m, 2H), 5.7-6.2 (m, 1H).
7. All the new compounds were characterized spectrometrically (IR, NMR, MS) and analytically.
8. (a) A by-product was the diene i (14%). (b) A mixture (ca 50%) of i and the recovered I was also obtained. (c) The major product was ii (47%). (d) The diene i (36%) was also formed. (e) The isolated product was iii (X = I) (87%). (f) The isolated product was iii (X = Cl) (31%) along with I (48%).



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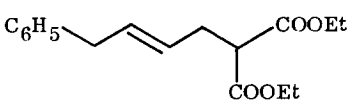

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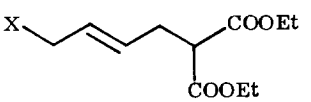
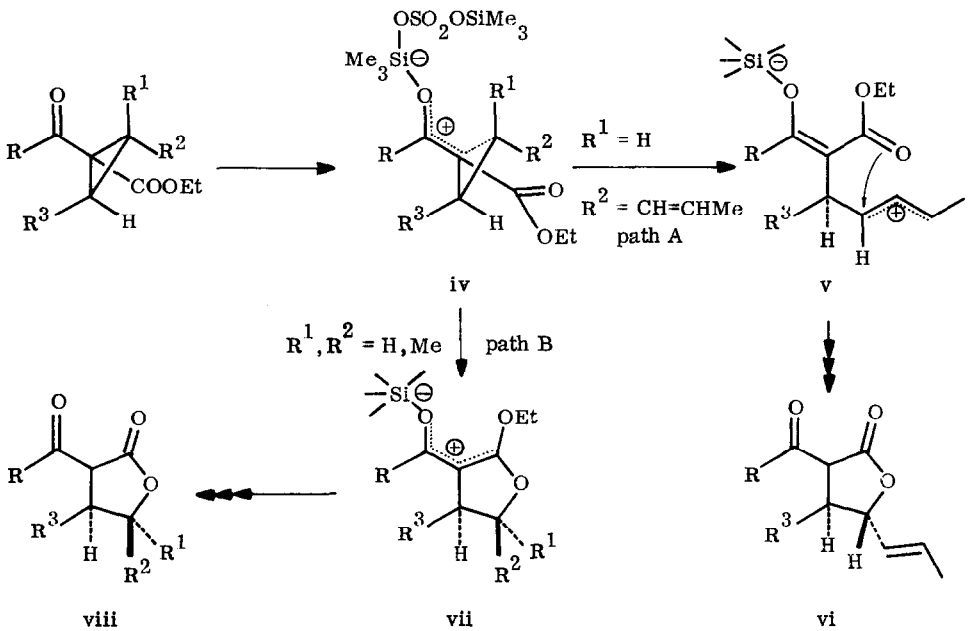


iii

9. D. E. McGreer and J. W. McKinley, Can. J. Chem., 51, 1487 (1973)
10. Inverse transformation, namely cyclopropanecarboxylate from γ-butyrolactone, was recently reported: S. Danishefsky, R. L. Funk, and J. F. Kerwin, Jr., J. Am. Chem. Soc., 102, 6889 (1980).
11. Bp 137-138° (bath temp)/0.06 Torr; IR: 1782, 1738, 966 cm^{-1}; MS: m/e 212 (M^+); ^{1}H-NMR ($CDCl_3$): δ 1.13 (d, J = 6.0 Hz, 3H), 1.35 (t, J = 6.9 Hz, 3H), 1.80 (d, J = 6.3 Hz, 3H), 2.53 (ddq, J = 6.0, 11.8, 10.4 Hz, Hb), 3.10 (d, J = 11.8 Hz, Ha), 4.24 (q, J = 6.9 Hz + dd (Hc), totally 3H), 5.51 (dd, J = 14.7, 7.2 Hz, 1H), 5.80 (dq, J = 14.7, 6.3 Hz, 1H). Stereochemical assignment is based on the ^{1}H-NMR data. See, W. Brügel, "Handbook of NMR Spectral Parameters," vol 1, Heyden and Son Ltd., London, 1979, p 245.

12. Accordingly, we may assume an intermediate which prefers W form of an allyl cation (cf. note 16). A recent communication refers to the stereochemistry of alumina-catalyzed oxa-vinylcyclopropane rearrangement proceeding with retention of the configuration at the migrating terminus. However, the conclusion should be suspended until the specificity is observed with respect to all stereoisomers of the substrate. M. E. Alonso and A. Morales, J. Org. Chem., 45, 4530 (1980)
13. J_{ab} = 6.7 Hz, J_{bc} = 6.7 Hz, J_{bd} = 3.1 Hz, J_{be} = 9.3 Hz. Examination of molecular models has led to the conclusion that the dihedral angle of H_a-C-C-H_b is almost the same as that of H_b-C-C-H_c with respect to VI, whereas the endo-propenyl isomer of VI is incapable of giving such set of coupling constants.
14. Bp 128-130° (bath temp)/0.03 Torr; MS: m/e 182 (M^+); ^{1}H-NMR ($CDCl_3$): δ 3.45 and 3.48 (a pair of doublets, J = 8.1 Hz), 4.2-4.4 (m, 0.18 H), 4.5-4.8 (m, 0.82 H). Upon irradiation at δ 1.78 the multiplet at higher field turned to doublet (J = 4.2 Hz) and the one at lower field to doublet of J = 5.0 Hz. The stereochemical assignment is based on the fact that the endo hydrogen in the bicyclic system appears at higher field than the exo one (see, F. A. Bovey, "NMR Data Tables for Organic Compounds," vol 1,John Wiley and Sons, New York, 1967, p 224, p 399-445; I. Tabushi, K. Fujita, and R. Oda, Tetrahedron Lett., 1967, 3755).
15. G. D. Andrews and J. E. Baldwin, J. Am. Chem. Soc., 98, 6705 (1976)
16. Following two competing pathways account for the observations. When R^2 is propenyl, path A will be the preferred one involving a zwitter ionic intermediate v which cyclizes to give the product vi exclusively. The substrate without 1-alkenyl group is not rewarded by such stabilization and, in turn, goes through path B to give an intermediate vii which then collapses to the product viii. The intermediacy of pentacoordinate silicon species such as iv, v and vii seems reasonable in view of such pentacoordinate silicon compounds isolated and well-documented: F. Klanberg and E. L. Muetterties, Inorg. Chem., 7, 155 (1968); F. P. Boer and J. W. Turley, J. Am. Chem. Soc., 91, 4134 (1969) and references cited therein. L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, 1965; H. Kwart and K. King, "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur," Springer-Verlag, Heidelberg, 1977, p 149.



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