Reductive Cleavage of Succinic Esters. A Method for the Introduction of Acetic Acid Fragments

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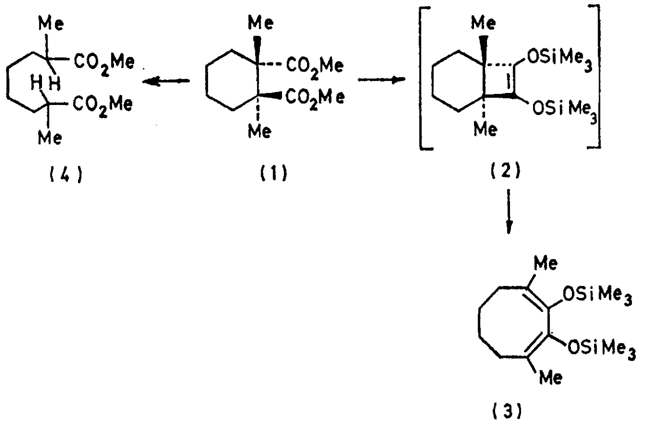
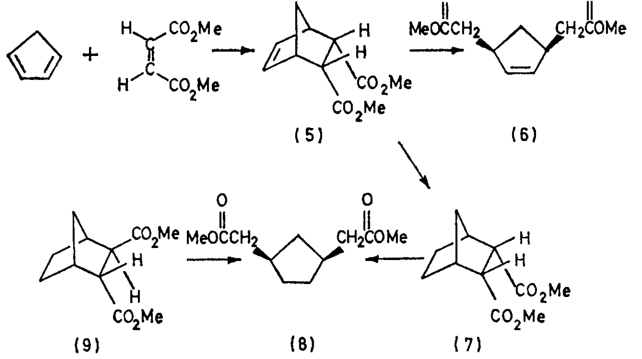
Summary Diels–Alder addition of maleic or fumaric esters to 1,3-dienes, followed by catalytic reduction and treatment with sodium in liquid ammonia at −78°, which promotes a solvent dependent reductive cleavage of the carbon–carbon σ bond of the succinic ester fragment, provides a general method for the preparation of derivatives of suberic acid.

Acyloin condensations have been carried out both in refluxing aromatic solvents with sodium or sodium–potassium alloy and in liquid ammonia with sodium. In an attempt to convert (**1**) into (**2**) *via* such acyloin condensations, we found that the products obtained were extremely dependent upon reaction conditions. Sodium in refluxing toluene in the presence of chlorotrimethylsilane gave an 88% yield of (**3**). Since (**3**) is an apparent thermal isomerization product of (**2**),[1] we reran the condensation at 25°, with sodium–potassium alloy in benzene. Again (**3**) was obtained as the only product. In contrast, when (**1**) was treated with sodium in liquid ammonia at −78°, neither (**2**) nor (**3**) was detected; instead, (**4**) was isolated in 54% yield. The formation of this product requires the reductive cleavage of the carbon–carbon σ bond of the succinic ester function. Although a few isolated examples of such a reductive cleavage are known,[2] the solvent dependency, generality, and synthetic utility of this reduction have not been appreciated.



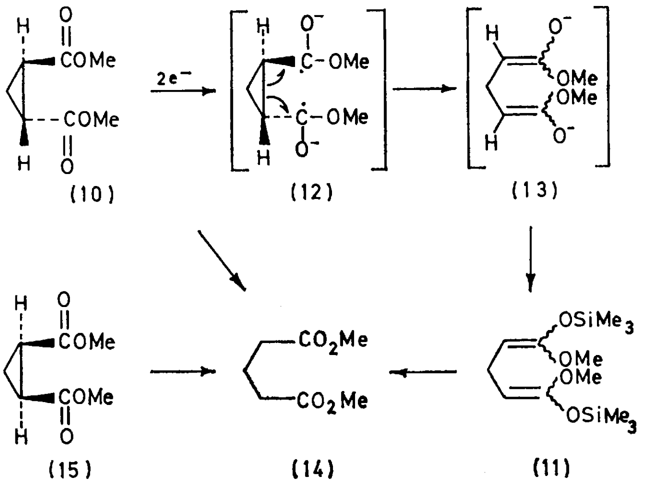
(4) (1) (2) (3)



(5) (6) (9) (8) (7)

Scheme

In principle, the reduction with sodium in liquid ammonia of succinic esters represents a method of introducing two acetic acid groups. Since succinic esters are readily prepared *via* addition of maleic esters or fumaric esters to 1,3-dienes, the process is one of adding acetic acid groups to the 1- and 4-positions of the conjugated diene (see Scheme). The Diels–Alder adduct formed from cyclopentadiene and dimethyl maleate yields 72% of (**6**) on reduction (Na–liq.NH_3) at −78°. Similarly, reduction



(10) (12) (13) (15) (14) (11)

(Na–liq.NH_3) of the saturated diester (**7**) gave (**8**) (52%). The same *cis*-diester (**8**) was obtained from similar reduction of the *trans*-diester (**9**).

Mechanistically, the cleavage appears to proceed *via* a two-electron addition to give a dianion diradical which cleaves to yield a bis-alkoxy-enolate. Evidence for this premise was provided by the trapping of such an enolate from the reductive cleavage of (**10**) by sodium in refluxing toluene containing chlorotrimethylsilane. Under these conditions (**10**) gave (**11**), presumably *via* (**12**) and (**13**). On addition of methanol, (**11**) gave (**14**). The diester (**14**) was also obtained as the only volatile product on reduction (Na–liq.NH_3) of either (**10**) or (**15**) at −78°.

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[1] J. J. Bloomfield, *Tetrahedron Letters*, 1968, 587, has reported the thermal isomerization of a related cyclobutene derivative.

[2] J. J. Bloomfield, *J.C.S. Chem. Comm.*, 1972, 96; E. Bertele, H. Boos, J. D. Dunitz, F. Elsinger, A. Eschenmoser, I. Felfer, H. P. Gribi, H. Gschwend, E. F. Meyer, M. Pesaro, and R. Scheffold, *Angew. Chem. Internat. Edn.*, 1964, **3**, 490; see also A. Eschenmoser, *Pure Appl. Chem.*, 1963, **1**, 302; J. J. Bloomfield, R. G. Todd, and L. T. Takahashi, *J. Org. Chem.*, 1963, **28**, 1474, and unpublished work referred to in footnote 2c therein.