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A NOVEL APPROACH TO *CIS*-CHRYSANTHEMIC ACIDS

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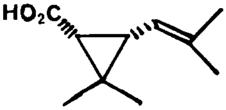
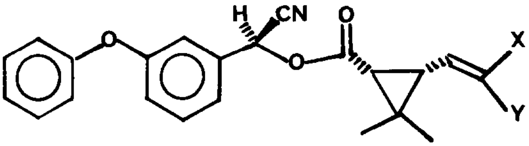
ABSTRACT: We describe a short route to (1*R*,3*S*)-*cis*-chrysanthemic acid (1) from the oxabicyclo[3.1.0]hexanone (3), itself derived from butenolide (4).

During the last few years there has been a burgeoning interest in the design of synthetic routes to (1*R*,3*S*)-*cis*-chrysanthemic acid (1) and derivatives.[1] This is not surprising given the potent insecticidal activity of the synthetic pyrethroids like deltamethrin (2a)[2] and cyhalothin (2b)[3], both of which contain analogues of (1). The naturally occurring pyrethrins contain (1*R*,3*R*)-*trans*-chrysanthemic acid moieties, and are much less potent insecticides, as are the synthetic pyrethroids with the same stereochemistry.[4]

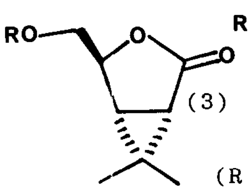


(1)

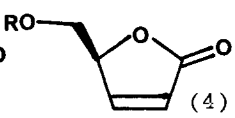


(2a) X=Y=Br (2b) X=Cl Y=CF_3

Our approach to (1) commences with the oxabicyclo[3.1.0]hexanone (3), and we have already described how this may be prepared via addition of diazopropane to butenolide (4) with subsequent photochemical elimination of nitrogen from the regioisomeric 4,5-dihydro-pyrazoles (5) and (6).[5]

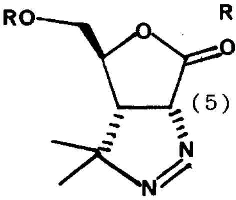


(3)



(4)

(R is $SiMe_2Bu^t$)



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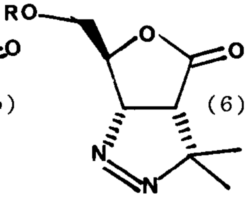
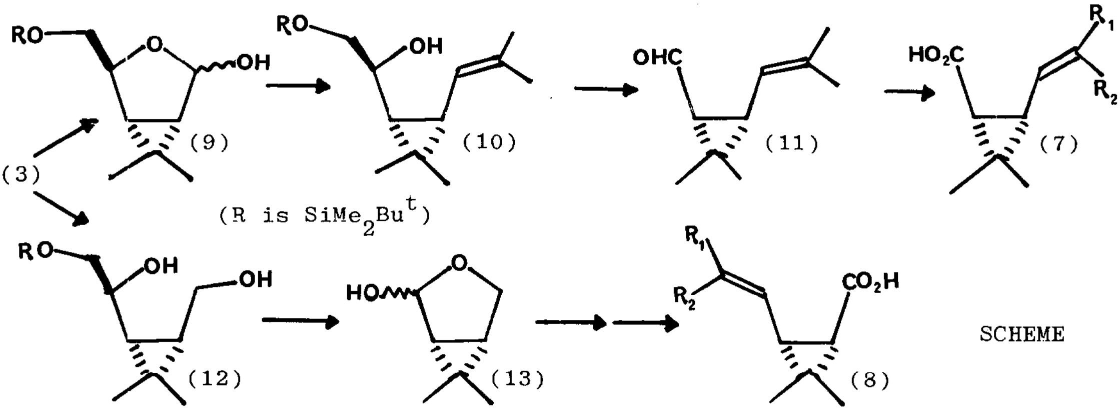


(6)

Compound (3) can, in principle, be converted into both (1*R*,3*S*)- and (1*S*,3*R*)-*cis*-chrysanthemic acids (7) and (8) via the sequences shown in the scheme. Reduction of lactone (3) to lactol(9)(DIBAL, toluene, -78°; quant.) was followed by a Wittig reaction ($Ph_3\overset{+}{P}CHMe_2Br^-$, BuLi, 5 eq. of each, RT; 83%) to yield alkenol (10).[6] Removal of the silyl group ($Bu_4\underset{+}{N}\underset{-}{F}$, THF; 94%), then cleavage of the resultant diol with periodate ($NaIO_4$, aq. THF, RT)



SCHEME

provided aldehyde (11) (94%). Oxidation of this sensitive aldehyde was best accomplished using sodium chlorite[7] in conjunction with a chlorine scavenger ($NaClO_2$,2-methyl-2-butene, aq. NaH_2PO_4, 1 hr., RT), and the desired acid (7) (R_1=R_2=Me) was isolated in excellent yield (95%). A similar sequence of reactions may be used to produce certain analogues, *e.g*. (7) (R_1=Me, R_2=CO_2Et) but not others (7) (R_1=R_2=halo). Alternatively, more forcing reduction of lactone (3) (excess DIBAL or $LiAlH_4$) yielded the triol derivative (12) (86%) and thence lactol (13) ($Bu_4\overset{+}{N}\overset{-}{F}$, THF; $NaIO_4$, aq. THF; 96%), a key intermediate for the production of the stereoisomeric chrysanthemic acids (8).

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(6) All compounds were fully characterised by IR, NMR, and high resolution mass spectrometry or by microanalysis. Comparisons with authentic samples were made where relevant, and an X-ray structure was obtained for compound (10).

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