Tetrahedron Letters,Vol.24,No.4,pp 423-424,1983 0040-4039/83/040423-02$03.00/0
Printed in Great Britain ©1983 Pergamon Press Ltd.

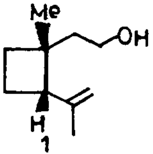
PHOTOLYSIS OF α-DIAZOCYCLOPENTANONES: RING CONTRACTION TO FUNCTIONALISED CYCLOBUTANES AND SYNTHESIS OF PRECURSORS TO GRANDISOL AND FRAGRANOL

Ujjal K. Banerjee and R.V. Venkateswaran*

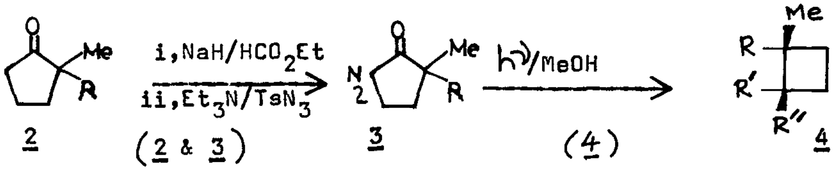
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India

Summary: Photolytic Wolff rearrangement of α-diazocyclopentanones (3a-c) in methanol leads to the cyclobutane carboxylates (4a-d).

The isolation and structure establishment of the important boll weevil pheromone, grandisol (1)[1], has generated a sustained interest towards its synthesis, leading to development of a variety of methods for the preparation of functionalised cyclobutanes[2]. The trans isomer of (1), termed fragranol[3] has also been isolated from nature.



1



(2 & 3)

a, R = Me
b, R = Ph
c, R = $CH_2.CH_2.OMe$

(4)

a, R = Me, R' = CO_2Me, R" = H
b, R = Ph, R' = CO_2Me, R" = H
c, R = $CH_2.CH_2.OMe$, R' = CO_2Me, R" = H
d, R = $CH_2.CH_2OMe$, R' = H, R" = CO_2Me
e, R = $CH{=}CH_2$, R' = CO_2Me, R" = H
f, R = $CH{=}CH_2$, R' = H, R" = CO_2Me

In a comprehensive approach aimed at the synthesis of this pheromone, we decided to investigate the potential of photolytic ring contraction of an appropriately substituted α-diazocyclopentanone for generation of the required cyclobutane synthon. Although such ring contraction of cyclopentanones to functionalised cyclobutanes has found wide applications in steroids[4] and other polycyclic systems[5], the extension of this procedure for ring contraction of simple cyclopentanones has not been explored. In this communication we report the application of this procedure for the ring contraction of a few representative α-diazocyclopentanones (3a-c) leading to the synthesis of the functionalised cyclobutanes (4a-d).

The α-diazoderivative (3a) of 2,2-dimethylcyclopentanone (2a), obtained in good yield through interaction of the corresponding formyl compound with tosyl azide[5b], was photolysed in methanol solution using a Hanovia 450W mercury lamp and on work-up followed by chromatography afforded in 40% overall yield (from 2a) the cyclobutane carboxylate (4a), ν 1725 cm^{-1}. δ 1.0(s,6H), 3.63 (s,3H). Similarly (3b), obtained from (2b), on photolysis, furnished essentially a single compound, assigned the cis structure (4b) from ^{1}H NMR. The methyl group in (4b) appeared as a singlet at δ 1.3 and it is expected that in the trans compound it will be shifted further upfield due to shielding from the ester group. This conclusions is further supported by an analogous one arrived at by Babler in his synthesis of grandisol, where the methyl group in the cis (4e) and trans (4f) compounds appeared at δ 1.34 and 1.13 respectively. Basic hydrolysis of (4b) followed by reesterification (diazomethane) furnished the same epimer (^{1}H NMR).

For the synthesis of grandisol, the disubstituted cyclopentanone (2c) was transformed to the α-diazoketone (3c) and subjected to photolysis in methanol. The product obtained in 36% overall yield lacked stereoselectivity and was found to be a Ca. 1:1 mixture of the cis (4c) and trans (4d) epimers from ^{1}H NMR (δ1.2,1.03 ,2s,3H; 3.2, 3.23, 2s,3H; 3.67,s,3H). This product mixture on basic hydrolysis and reesterification (diazomethane) led only to product retaining the same epimeric composition (^{1}H NMR). The isomeric esters (4c) and (4d) are potential synthons towards grandisol and fragranol.

We are currently studying the effect of solvent and structural variation on substrate to probe fully the stereochemical outcome in this ring contraction leading to substituted functionalised cyclobutanes and complete the synthesis of grandisol and fragranol.

We wish to thank Dr. S. Lahiri for assistance in the photochemical experiments and Professor U.R. Ghatak for his interest in this work.

References:

1 J.H. Tumlinson, D.D. Hardee, R.C. Gueldner, A.C. Thompson, P.A. Hedin and J.P. Minyard, SCIENCE, 166, 1010 (1969)

2 (a) J.A. Katzenellenbogen, SCIENCE, 194, 139 (1976). (b) V. Rautenstrauch, J.CHEM.SOC., CHEM. COMMUN., 519 (1978). (c) K. Mori, TETRAHEDRON, 34, 915 (1978). (d) R.D.Clarke, SYNTH. COMMUN., 325 (1979)

3 F. Bohlman, C. Zdero, and N. Faas, CHEM. BER., 106, 2904 (1973)

4 (a) M.P. Cava and E. Moroz, J. AMER. CHEM. SOC., 115 (1962). (b) J. Meinwald and A.J. Taggi, J. AMER. CHEM. SOC., 95, 7663 (1973) and references cited therein

5 (a) P.E. Eaton and G.H. Temme III, J. AMER. CHEM. SOC., 95, 7508 (1973). (b) K.B. Wiberg, B.L. Furtek, and L.K. Olli, J. AMER. CHEM. SOC., 101, 7675 (1979). (c) W.G. Dauben and D.M. Walker, TETRAHEDRON LETTERS, 711 (1982)

6 J.H. Babler, TETRAHEDRON LETTERS, 2045 (1975)

(Received in UK 19 October 1982)