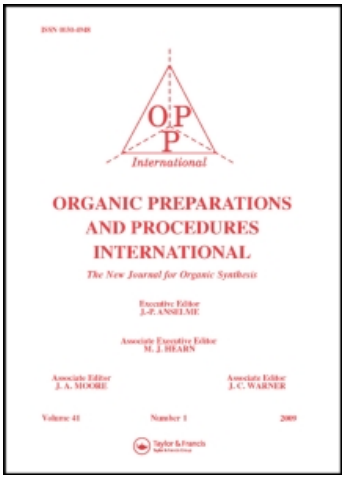


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

CHEMOSELECTIVE CATALYTIC HYDROGENATION OF CARBONYL CONJUGATED DOUBLE BONDS IN THE PRESENCE OF STYRENOID BONDS IN BICYCLO[3.3.1]NONADIENONES

R. Chakraborti[a]; B. C. Ranu[a]; U. R. Ghatak[a]
[a] Depamnent of Organic Chemistry, Indian Association for the Cultivation of Science, Calcutta, INDIA

To cite this Article Chakraborti, R. , Ranu, B. C. and Ghatak, U. R.(1989) 'CHEMOSELECTIVE CATALYTIC HYDROGENATION OF CARBONYL CONJUGATED DOUBLE BONDS IN THE PRESENCE OF STYRENOID BONDS IN BICYCLO[3.3.1]NONADIENONES', Organic Preparations and Procedures International, 21: 3, 377 — 380
To link to this Article: DOI: 10.1080/00304948909356405
URL: http://dx.doi.org/10.1080/00304948909356405

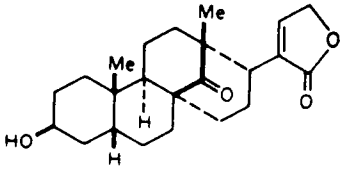
CHEMOSELECTIVE CATALYTIC HYDROGENATION OF CARBONYL CONJUGATED DOUBLE BONDS IN THE PRESENCE OF STYRENOID BONDS IN BICYCLO[3.3.1]NONADIENONES

Submitted by (03/10/88)

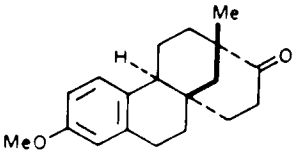
R. Chakraborti, B. C. Ranu and U. R. Ghatak*

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

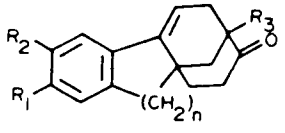
During a reinvestigation of the cardiac glycosides from Nerium, Abe and Yamauchi[1] isolated a few new cardinolides having a novel bicyclo[3.3.1]nonan-9-one carbocyclic framework 1. Recently, we developed[2] a remarkably simple formylation-cyclization route to functionalized bicyclo[3.3.1]nonane derivatives. The styrenoid ketones 3b or 5b, thus obtained,[2c] appeared to be promising precursors for the elaboration to the tetracyclic ketone 2 as a starting point for the synthesis of the difficultly accessible carbocyclic framework of 1. This objective prompted us to study in detail the stereochemical outcome of the reduction of 3b and 5b and the related tetracyclic systems (3a-d, 4a-d)[2a,2c] and (5a-d, 6a-d).[2a,2c]



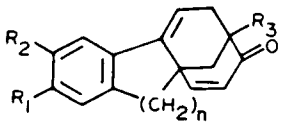
1



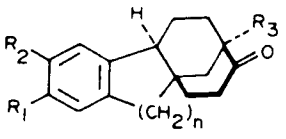
2



3, n = 2
4, n = 1



5, n = 2
6, n = 1



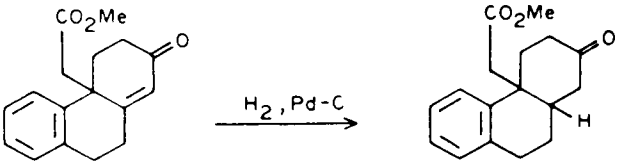
7, n = 2
8, n = 1

a) $R_1 = R_2 = H$, $R_3 = Me$ b) $R_1 = OMe$, $R_2 = H$, $R_3 = Me$

c) $R_1 = H$, $R_2 = OMe$, $R_3 = Me$ d) $R_1 = OMe$, $R_2 = R_3 = H$

When the styrenoid bond in the ketone 3b was hydrogenated over 10% Pd/C in ethanol or ethyl acetate at one atmospheric pressure and room temperature, to our dismay, the undesired trans-saturated ketone 7b[3] was obtained as the sole product. Similar hydrogenation of styrenoid ketones 3a, 3c,3d and 4a, b gave the saturated ketones 7a, 7c, 7d and 8a-b whose stereochemistry at the benzylic center was assigned by analogy with 7b.

In an earlier observation[4] from this laboratory, the catalytic hydrogenation of the enone 9 using Pd/C (10%) in pyridine at room temperature and atmospheric pressure led exclusively to the



9 10

cis-product 10. Attempted reduction of the styrenoid double bond of 3b with Pd/C (10%) using pyridine or piperidine led to the complete recovery of the starting material. However, hydrogenation of the styrenoid enone 5b under identical conditions gave the ketone 3b exclusively through selective reduction of the carbonyl conjugated double bond. Piperidine was found to be considerably superior to pyridine as the latter underwent simultaneous reduction making the overall hydrogenation more complex. Although other basic solvents such as N-methylpiperidine, γ-picoline, collidine and pyrrolidine were also effective, piperidine was found to be the solvent of choice. Thus, when the other carbonyl conjugated ketones 5a, 5c, 5d and 6a-b were subjected to hydrogenation under the same conditions in piperidine, the known styrenoid ketones 3a, 3c, 3d and 4a-b were obtained in excellent yields. On the other hand, when 5a-d and 6a, b were hydrogenated with Pd/C (10%) in ethanol, the saturated ketones 7a-d and 8a-b were produced in quantitative yields.

In conclusion, though the catalytic hydrogenation of the styrenoid ketones 3b and 5b failed to give the desired stereoisomer 2, the present study introduces a method for chemoselective reduction of carbonyl conjugated double bond and stereoselective hydrogenation of styrenoid double bond, which may find application in natural product synthesis.

EXPERIMENTAL SECTION

Mps. were recorded on a Mettler FP-16 instrument and are uncorrected. IR spectra of solids (KBr) and liquid (neat) were recorded on a Perkin-Elmer model PE298. ^{1}H NMR spectra were recorded at 60 MHz on Varian Associates T-60 A or at 200 MHz on Varian XL-200 for solutions in CCl_4 or $CDCl_3$, with TMS as internal standard. Column chromatography was performed on neutral alumina (B. D. H. India). Petroleum refers to the fraction boiling between 60-80° and light petroleum refers to the fraction boiling between 40-60°. Elemental analyses were performed in this laboratory by Mr. P. P. Bhattacharyya.

Stereoselective Reduction of Styrenoid Double Bonds. Preparation of Saturated Ketones (7a-d) and (8a-b) from (3a-d/5a-d) and (4a-b/6a-b).- The enones and dienones were hydrogenated in ethanol using Pd/C (10%) by standard procedure.[2e]

Chemoselective Hydrogenation of Carbonyl Conjugated Double Bond Using Palladium-Charcoal in Piperidine. Preparation of Enones (3a-d) and (4a-d) from (5a-d) and (6a-b). General Procedure.- The dienone (100 mg) was hydrogenated in dry piperidine (3 ml) in presence of

10% Pd/C (20 mg) at room temperature and atmospheric pressure for 2 hrs. The catalyst was then removed by filteration and the solution was diluted with ice-cold 2N HCl (25 ml) and extracted with ether (3 x 20 ml). The ethereal extract was washed with brine and dried (Na_2SO_4). Evaporation of solvent left a solid in nearly quantitative yield which was purified by crystallization from petroleum to furnish a pure sample.

Compounds (3a-c) and (4a-b) were characterized by comparison with authentic samples[2a-2c] (mp, mmp, IR and ^1H NMR). The enone (3d), mp 107° (petroleum), was characterized by its spectral data. UV (EtOH) λ_{max} 264 nm (log ε 4.35); IR (KBr): 1710, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz): δ 1.4-2.96 (m, 13H), 3.8 (s, 3H), 6.30 (t, 1H, J = 4 Hz), 6.63-6.83 (m, 2H), 7.60 (d, 1H, J = 9 Hz).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.69; H, 7.59.

TABLE 1. Physical and Spectral Data of Saturated Ketones (7a-d) and (8a-b).

Cpd	mp. (°C)	IR (cm^{-1})	^1H NMR (δ)	Elemental Analysis
7a	95-96 (light petroleum)	1702	($CDCl_3$, 60 MHz) 1.09 (s,3H), 1.31-3.1(m,15H), 7.05-7.21(m,4H)	Calcd : C, 84.99; H, 8.72 Found: C, 84.86; H, 8.77
7b	135 (petroleum)	1700 1609	(CCl_4, 60 MHz) 1.01 (s, 3H),1.21-2.81(m,15H), 3.70(s,3H),6.45-7.05 (m,3H)	Calcd : C, 80.24; H, 8.51 Found: C, 80.24; H, 8.51
7c	132 (light petroleum)	1695 1605	($CDCl_3$, 200 MHz) 1.08 (s,3H),1.40-2.92 (m,15H), 3.80(s,3H), 6.70-7.06 (m,3H)	Calcd : C, 80.24; H, 8.51 Found: C, 80.29; H, 8.81
7d	97-98 (petroleum)	1700 1600	($CDCl_3$, 200 MHz) 1.26-2.96 (m,15H), 3.78 (s, 3H), 6.66-6.80 (m,2H), 7.16 (d,1H,J=9 Hz)	Calcd : C, 79.96; H, 8.20 Found: C, 80.05; H, 8.15
8a	oil	1690 1595	($CDCl_3$, 200 MHz) 0.94 (s,3H), 1.18-3.20(m,13H), 7.14-7.21(m,4H)	Calcd : C, 84.95; H, 8.39 Found: C, 84.70; H, 8.45
8b	80-81 (methanol)	1695 1600	($CDCl_3$, 200 MHz) 0.94 (s,3H), 1.14-3.16 (m, 13H), 6.74-8.12 (m,3H)	Calcd : C, 79.96; H, 8.20 Found: C, 80.09; H, 8.07

REFERENCES

1. F. Abe and T. Yamauchi, Chem. Pharm.Bull. Japan, 27, 1604 (1979).

2. a) U. R. Ghatak, B. Sanyal, S. Ghosh, M. Sarkar, M. S. Raju and E. Wenkert, J. Org. Chem., 45, 1081 (1980).

b) R. Dasgupta, B. C. Ranu, and U. R. Ghatak, Indian J. Chem., 22B, 619 (1983).
c) R. Chakraborti, B. C. Ranu and U. R. Ghatak, J. Org. Chem., 50, 5268 (1985).
d) Idem, Synth. Commun., 17, 1539 (1987).
e) B. C. Ranu, R. Chakraborti and U. R. Ghatak, J. Chem. Soc. Perkin Trans. 1, 795 (1988).

3. The sterochemistry of this ketone was established by direct comparison with an authentic sample prepared by ring expansion[2d] of (±)-1,2,3,4,4aα,9,10,10a-octahydro-7-methoxy-2α -methyl-11-oxo-2β, 10aβ-ethanophenanthrene [P. N. Chakrabortty, R. Dasgupta, S. R. Ghosh and U. R. Ghatak, Tetrahedron, 28, 4653 (1972)].

4. G. Sinha, S. K. Maji, U. R. Ghatak, M. Mukherjee, A. K. Mukherjee and A. K. Chakravarty, J. Chem. Soc. Perkins Trans. 1, 2519 (1983).

****

PREPARATION OF NOVEL

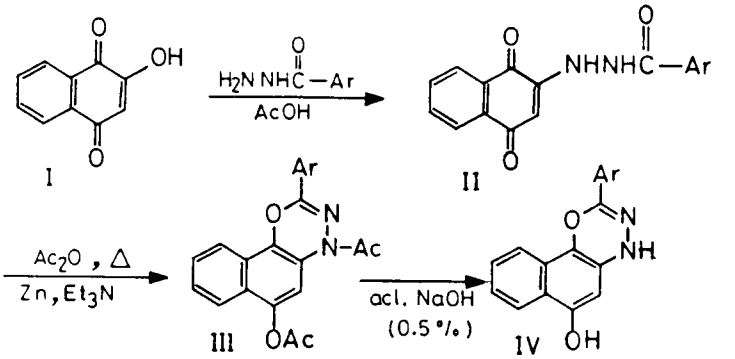
2-ARYL-4H-NAPHTH[2,1-e]-1,3,4-OXADIAZINE- 6-OL DERIVATIVES

Submitted by (04/12/88)
R. Ashok Kumar and C. K. Kokate
University College of Pharmaceutical Sciences
Kakatiya University, Warangal 506 009, INDIA

and

M. S. Rao and T. V. Padmanabha Rao
Department of Chemistry, Kakatiya University
Warangal 506 009, INDIA

As a continuation of our earlier work on heterocyclic systems from natural quinones,[1-4] we are now reporting the preparation of novel heterocyclic system namely 2-aryl-4H-naphth[2,1-e]-1,3,4-oxadiazine-6-ol (IV) in a three-step process from Lawsone, a natural quinone, in good yields. Lawsone (I, extracted from Lawsonia alba) was first treated in acetic acid with aroylhydrazines to give 2-aroyl-hydrazino-1,4-napthoquinone (II) in excellent yields.



As the attempts for direct cyclization of II to give the title products failed under various