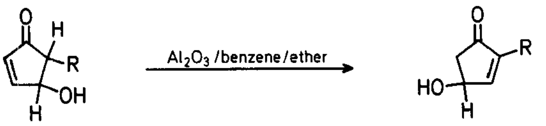
A Simple Conversion of 4-Substituted 5-Hydroxy-3-oxocyclopentenes into the 2-Substituted Analogs

G. Piancatelli, A. Scettri

Istituto di Chimica Organica dell'Università di Roma, P. delle Scienze 5, I-00185 Roma, Italia

The substituted 3-oxocyclopentenes and their 5-hydroxy derivatives are major synthons for several important natural products, such as *cis*-jasmone, rethrolone, and the prostaglandins; this fact gives rise to considerable interest in developing synthetic routes to these compounds[1].

Recently, we have described a new and efficient two-step synthesis of 5-hydroxy-3-oxocyclopentene 4-derivatives (**1a–c**)[2] by the acid-catalyzed molecular rearrangement of the corresponding 2-furylmethanols, which are obtained from the normal Grignard reaction of furan-2-carboxaldehyde with alkyl-(or phenyl-)magnesium bromide[3]. We have now achieved a simple and convenient one-step conversion of compounds **1a–c** to the racemic 2-substituted 5-hydroxy-3-oxocyclopentenes **2a–c**.



1a R = C_6H_5
b R = n-C_6H_{13}
c R = CH_3

2a-c

This conversion takes place during column chromatography of compounds **1** on neutral (for **1a**) or basic (for **1b, c**) alumina in benzene/ether (4:1): the stable compounds **2a–c** are isolated in 85–95% yield. The analytical and spectrometric data of compounds **2a–c** are in accord with the proposed structures. In particular, in the ^{1}H-N.M.R. spectrum of

Table. 2-Substituted 5-Hydroxy-3-oxocyclopentenes (**2**) from the **4-Substituted** Analogs (**1**)

Product	Yield [%]	Empirical formula[a]	n_D^{23}	I.R. (neat)[b] ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$)[b] δ [ppm]
2a	90	$C_{11}H_{10}O_2$ (174.2)	(m.p. 58–59°, from hexane)	1710 (C=O); 1600 (C=C)	7.58 (m, 2H$_{arom}$); 7.51 (d, 1H, 1-H, J=3Hz); 7.32 (m, 3H$_{arom}$); 4.93 (m, 1H, 5-H); 3.2 (broad s, 1H, —OH); 2.91 (dd, 1H, 4-H, J_1=18Hz, J_2=6Hz); 2.4 (dd, 1H, 4-H, J_1=18Hz, J_2=2Hz)
2b	95	$C_{11}H_{18}O_2$ (182.3)	1.4808	1710 (C=O); 1635 (C=C)	7.14 (m, 1H, 1-H); 4.9 (m, 1H, 5-H); 3.3 (broad s, 1H, —OH); 2.8 (dd, 1H, 4-H, J_1=18Hz, J_2=6Hz); 2.28 (dd, 1H, 4-H, J_1=18Hz, J_2=2Hz); 2.14 (m, 2H, allylic —CH$_2$—); 1.3 (sharp s, 8H, 4 —CH$_2$—); 0.86 (t, 3H, —CH$_3$)
2c	85	$C_6H_8O_2$ (112.1)	1.4895	1710 (C=O); 1640 (C=C)	7.22 (m, 1H, 1-H); 4.9 (m, 1H, 5-H); 3.4 (broad s, 1H, —OH); 2.82 (dd, 4-H, 1H, J_1=18Hz, J_2=6Hz); 2.24 (dd, 1H, 4-H, J_1=18Hz, J_2=2Hz); 1.83 (d, 3H, —CH$_3$, J=1Hz)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.18; H, ±0.19.

[b] The I.R.- and ^{1}H-N.M.R. data are consistent with those reported for similar compounds[4].

2a the proton at C-5 shows a complex multiplet at δ=4.93; by double irradiation at δ=7.51 (H$_{olefin}$ at C-1), it turns into a dd (J_1=6Hz, J_2=2Hz), which is completely in accord with the presence of the group —CO—CH$_2$—CH(OH)—CH=C(R)—.

2-Substituted 5-Hydroxy-3-oxocyclopentenes (2) from the 4-Substituted Analogs (1):

Compound **1** (1 g, prepared according to Ref.[3]) is column-chromatographed on alumina (100g; Brockmann Grade III, neutral for **1a**; Brockmann Grade III, basic for **1b, c**) using benzene/ether (4:1) as eluent. The products **2a–c** are obtained as colorless oils which are pure and free from starting material by T.L.C. (silica gel, benzene/ether 1:1).

We are grateful to the Italian C.N.R. for financial support.

Received: July 1, 1976
(Revised form: September 10, 1976)

---

[1] R. A. Ellison, *Synthesis* **1973**, 397.

[2] Compounds **1a–c** were obtained as racemic mixtures of only one pair of enantiomers (4*R*, 5*S* and 4*S*, 5*R*).

[3] G. Piancatelli, A. Scettri, S. Barbadoro, *Tetrahedron Lett.* **1976**, 3555.

[4] K. Ogura, M. Yamashita, G. Tsuchihashi, *Tetrahedron Lett.* **1976**, 759.