Pergamon

Tetrahedron Vol. 50, No. 9, pp. 2895-2906, 1994

0040-4020/94 $6.00+0.00

0040-4020(93)E0220-A

A Simple Method for the Preparation of Various 1-Oxo-hydrindene-2-acetic and -propionic Acids. Valuable Precursors of Strigol and Its Analogues

*István Kádas, Géza Árvai, László Tőke**

Research Group of the Hungarian Academy of Science, Department of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest P.O.B. 91, Hungary

Gábor Tóth, Áron Szöllősy

Technical and Analytical Research Group of the Hungarian Academy of Science, Institute for General and Analytical Chemistry, Technical University of Budapest, H-1111 Budapest Gellért tér 4, Hungary

Mária Bihari

Chemical Works Gedeon Richter Ltd. H-1475 Budapest 10 P.O.B 27, Hungary

Abstract: *An improved annulation sequence is presented, making use of the one-pot cyclization of 5-nitropentan-2-one and cyclopent-2-enone diesters to afford 7-methyl-4-nitro-1-oxohydrindene derivatives. Functional group elaborations of these intermediates lead to a series of the title compounds, which could be readily converted to the tricyclic moieties of strigol and its analogues of biological importance.*
Keywords: *Annulation; Cyclopent-2-enone derivatives; Michael reaction; 5-Nitropentan-2-one; Strigol*

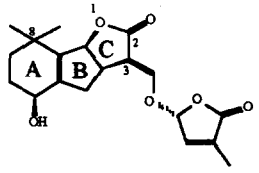
INTRODUCTION

Strigol (**1**), isolated from root exudates of Gossypium hirsutum (cotton), is a potent germination stimulant to parasitic Striga species[1]. These pests cause severe damage to graminaceous crops of great economic interest including sorghum, millet, rice and sugarcane. Strigol and its effective analogues can be used to eradicate these harmful weeds by triggering suicidal germination[2] of their dormant seeds in the absence of suitable host plant.

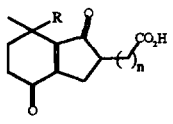
This attractive idea prompted several practical syntheses[3] of strigol to provide a sample for field testing. Most of the reported synthetic schemes targeted the preparation of 7,7-dimethyl-1,4-dioxo-hexahydroindene acetic acid (**2a**), which can easily be converted to the ABC fragment of strigol via standard procedures[4,3c].

In our project we undertook to improve the B→AB annulation cruical in the formation of hydrindene skeleton. Efforts were also aimed at extending the method toward C-ring homologues with or without modification in the A-ring. We envisaged that annulation with 5-nitropentan-1-one[5,6] could be applicable to cyclopent-2-enone diesters (**6a,b**) as well. In this way, the incorporation of carboxy-alkyl side chain - which serves as a precursor of the C-ring - at an early stage of the synthesis would render our approach more convergent and efficient. Furthermore, exploiting the versatile reactivity of the enedione system of hydrindene derivatives **8a,b** thus prepared can provide pathways favourable for the synthesis of

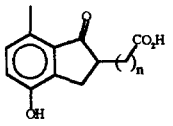
various strigol analogues. In this paper we present our results on this synthetic scheme opening access to C-homostrigols and 8-norstrigols, too.



1



2-3	n	R
2a	1	Me
2b	2	Me
3a	1	H
3b	2	H

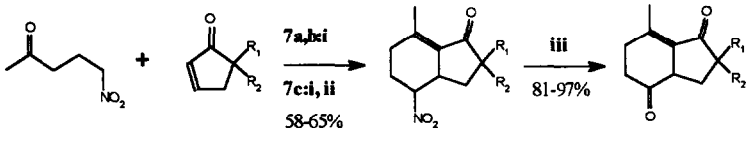


4a n=1
4b n=2

Fig. 1.

RESULTS AND DISCUSSION

The key step in our approach is an efficient annulation reaction with 5-nitropentan-2-one (**5**) on cyclopent-2-enone diesters **6a,b**. Raphael et al. reported[5,6] the Michael reaction of **5** with cyclopent-2-enone (**6c**) and 5,5-dimethylcyclopent-2-enone (**6d**) catalyzed by i-Pr_2NH and n-Bu_4NF, respectively. The corresponding Michael adducts were submitted to an intramolecular aldol condensation in a separate step to furnish 4-nitro-hydrinden-1-ones (**7c,d**) (Fig. 2.).



5 **6a-d** **7a-d** **8a,b**

	R_1	R_2
a	CO_2Me	CH_2CO_2Et
b	CO_2Me	$(CH_2)_2CO_2Me$
c	H	H
d	Me	Me

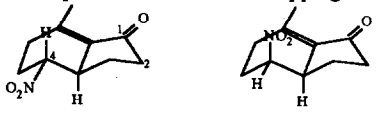
i: 0.1 eq. t-BuOK, t-BuOH, reflux, 6 h
ii: p-TsOH, benzene, reflux, 3.5 h
iii: 1.) NaOMe, MeOH, THF
2.) $TiCl_3$, NH_4AcO

Fig. 2.

However, we found that under certain conditions (0.1 eq t-BuOK in t-BuOH at reflux temperature, 6h) the bicyclic nitro compounds **7a,b** required for our purposes can be isolated in a one-pot process as the sole product. Namely, the primary Michael adduct underwent aldol condensation smoothly and **7a,b** were isolated in good yield. Moreover, formation of only two of the four possible diastereomers was observed. Though the stereogenic centers of **7a,b** are destroyed in the course of the synthesis, it was of interest to study their stereochemistry. For this purpose, the known 4-nitro-7-methylhydrinden-1-one (**7c**) was chosen as a model compound, since both diastereomers are available from the reaction of nitropentanone **5** with

cyclopent-2-enone and their separation can easily be achieved[5]. Nevertheless, no assignation of their relative configuration has been attempted yet.

For differentiation of the *trans* (3aRS,4RS) and *cis* (3aRS,4SR) diastereomers of **7c** (Fig. 3.), chemical shifts of C-4, C-5, C-6 and H-4 and the splitting pattern of H-4 proved to be helpful (see Table). The less polar major isomer (m.p. 87-88°C) was assigned *trans*, whereas the oily isomer the *cis* relative configuration. Similarly, considering the chemical shifts of H-4 and C-4 and the values of $^3J(H_{ax}\text{-}4, H_{ax}\text{-}3a)$ and $^3J(H_{ax}\text{-}4, H_{ax}\text{-}5)$ (12.5 and 10.5 Hz, respectively), the predominant stereoisomers of **7a,b** possess *trans* diaxial H-4 and H-3a, and the minor isomers differ only in the configuration of C-2. In the case of **7a** the major stereoisomer was separated by crystallisation. Its relative configuration at C-2 could not be unambiguously determined by NOE experiments due to overlapping ^{1}H-NMR signals of H_{eq}-3 and CH_2-2.



trans-**7c** *cis*-**7c**

Fig. 3 .

Table. Characteristic ^{1}H and ^{13}C Chemical Shifts (ppm) of **7a**, **7b**, **7c** (250 MHz, $CDCl_3$)

	trans-**7a**		*trans*-**7b**		**7c**	
	major	minor	major	minor	*trans*	*cis*
C-3a	40.1	38.9	39.2	40.2	42.9	40.7
C-4	86.8	86.7	86.6	86.8	87.2	81.5
C-5	27.0	27.2	27.3	27.0	27.5	25.5
C-6	32.9	32.8	33.1	33.5	32.9	29.4
H-4	4.31	4.39	4.35	4.24	4.32	5.10
H-3a	3.50	3.27	3.28	3.36	3.20	3.04

The 3a,4-*trans* selectivity observed in the case of **7a,b** is explained by equilibration to the most stable *trans* diastereomers with equatorial substituents, as shown by converting *cis*-**7c** to *trans*-**7c** on treatment with t-BuOK in refluxing t-BuOH.

The nitro compounds **7a,b** were then cleanly converted to the corresponding enediones **8a,b** on successive treatment with sodium methoxide and buffered aqueous solution of titanium(III)-chloride[7]. Neither double-bond isomerization nor ester hydrolysis were observed during the modified Nef reaction.

Enediones **8a,b** are considerably unstable in strong acidic or basic medium. They readily undergo double-bond isomerization to the fully conjugated system (such as in **3a,b**, Fig. 4.) or spontaneous aromatization occurs in the presence of air[6]. Namely, hydrolysis and decarboxylation of **8a,b** was accomplished with aq. $Ba(OH)_2$/air[8], with concomitant aromatization to furnish the 7-methyl-4-hydroxyindan-1-one carboxylic acids **4a,b** in 47-50% yield.

On the other hand, when applying mild conditions to the hydrolysis of **8a,b** (5% aq. H_2SO_4 in DME under inert atmosphere) aromatization was avoided and the 7,7a-double-bond isomerized to the 3a,7a-positions to give the carboxylic acids **3a,b** in good yield (Fig. 4.).

Moreover, **8a** and **8b** were transformed to the strigol and C-homostrigol precursors **2a** and **2b**, respectively, via a 3-step pathway (Fig. 4.). Introduction of the methyl group in 7-position was achieved by 1,4-conjugate addition of $LiMe_2Cu$ to the protected enediones **9a,b**. No interference of the ester groups was observed during this reaction. When the pure diastereomer of **7a** was used in the reaction sequence, ketal **10a** was obtained as a 9:1 mixture of diastereomers, the major being the *trans*-hydrindane-1-one derivative. Oxidative hydrolysis and decarboxylation of **10a,b** (AcOH, cc. HCl, reflux in O_2 atmosphere) gave the desired 7,7-dimethyl-1,4-dioxohexahydroinden-2-carboxylic acids **2a,b** in reasonable yield.

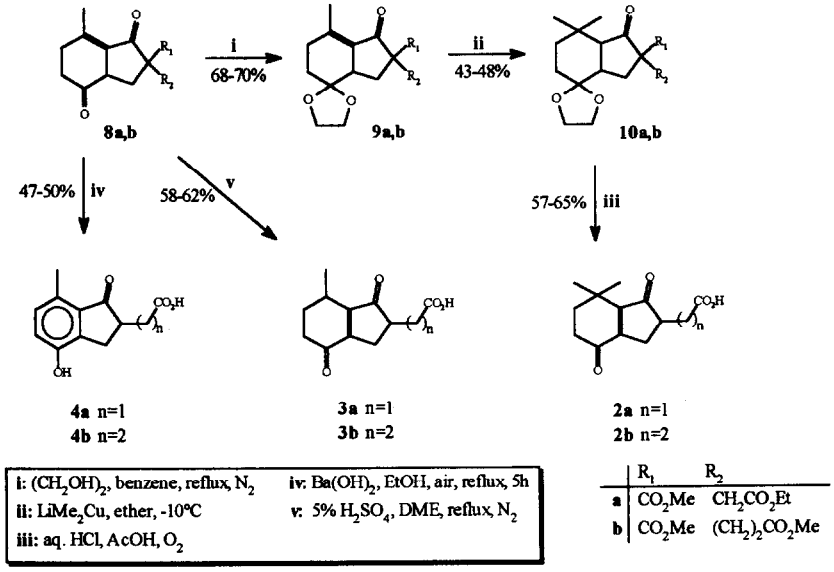


Fig. 4.

With the indan-1-one propionic acid **4b** in our hands as a model compound of C-homostrigol with no additional stereogenic centers, we studied the formation and stereochemistry of the δ-lactone ring. It is well documented in the literature[9,10] that indan-1-one-2-acetic acid derivatives, such as **4a**, are reduced with $NaBH_4$ in aq. NaOH and the *trans*-hydroxy acid **11a** is isolated as the major isomer (Fig.5.). The *trans* selectivity is either attributed to steric approach control or explained in terms of product development control[11]. Namely, the predominant stereoisomer produced is the more stable of the two isomers, provided that the substrate is a sterically unhindered ketone.

On reduction of indan-1-one propionic acid **4b** with $NaBH_4$, the *trans*-hydroxy acid **11b** was obtained in good yield, isolated after a rapid extractive work-up of the reaction mixture that was carefully brought to pH 3-4. The predominant formation of the *trans* isomer may be explained by kinetic control due

to interaction of the borohydride reagent with the carboxyl group and orientation of the hydride attack on the same side where the carboxyalkyl chain resides[9].

The *trans*-1,4-dihydroxy-7-methylindan-2-acetic acid (**11a**) can easily be cyclized to the *cis*-γ-lactone **12a** on acidifying the solution of its sodium salt to pH 1[10]. Adopting this method to *trans*-**11b**, prolonged acidic treatment yielded only a mixture of *cis*-δ-lactone **12b** and *trans*-hydroxy acid **11b** (in a ratio of ca. 1.35:1), with the concomitant formation of a small amount of the *cis*-hydroxy acid **11b** resulting from epimerization at C-1.

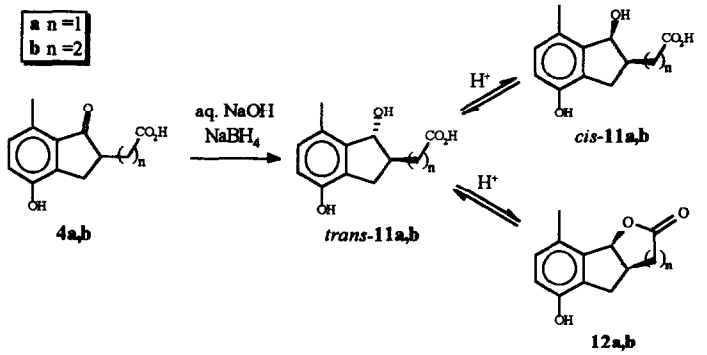


Fig. 5.

Considering these findings, one can suppose that the *cis*-lactone **12b** arises from *trans*-**11b** via intramolecular A_{Al} mechanism, that is, the nucleophilic displacement of the protonated hydroxyl group by the carboxyl oxygen leads exclusively to *cis*-annulation. This route is also supported by an experiment, in which the *cis*-lactone ring was opened to give solely *trans*-**11b** by dissolving the lactone in aq. NaOH then acidifying the mixture to pH 3-4.

The geometry of the isolated products **11b**, **12b** and **12a** were established by NOE measurements and elucidation of the NMR spectra of the lactones was achieved by heteronuclear COSY experiments.

Several attempts were made to complete the lactonization of *trans*-**11b**. DCC and its water soluble derivatives resulted only in complex reaction mixtures. Similarly, p-TsOH in benzene and p-TsCl/DMAP in pyridine, turned out to be futile experiments. The interference of the phenolic hydroxyl group might cause the difficulties, so derivatization of this group is currently under investigation in our laboratory.

In conclusion, we have shown a facile and variable synthetic route to a series of hydrindene carboxylic acids **2-4**, which could readily be converted to the tricyclic moieties of strigol and its analogues. The model study of the lactonization of 1,4-dihydroxy-7-methylindan-2-yl propionic acid (**9b**) provided a good background to the synthesis of C-homostrigol.

EXPERIMENTAL PART

Methods. Column chromatography was performed using Merck Kieselgel 60, 70-230 mesh, TLC on alumina sheets coated with Kieselgel 60 F_{254}. Plates were stained with anisaldehyde solution (100 ml glacial acetic acid, 2ml cc. sulfuric acid and 1 ml anisaldehyde) and heated at ca. 150°C. IR spectra were measured on a SPECORD75 IR and NICOLET FT-IR instruments. ^{1}H-NMR and ^{13}C-NMR spectra were

recorded in $CDCl_3$, chemical shifts are given on the δ-scale (δ_{TMS}=0 ppm). Mass spectra were taken on a VG TRIO-2 mass spectrometer (EI mode, 70 eV).

Materials. Technical grade solvents were purified by standard methods. 5-Nitropentan-2-one was prepared according to the method of Clark and Cork[12].

Ethyl 1-methoxycarbonyl-2-oxocyclopent-3-en-1-ylacetate (6a)

A solution of ethyl 3-bromo-1-methoxycarbonyl-2-oxocyclopent-1-ylacetate[13] (30.7 g, 0.1 mol) in lutidine (120 ml) was refluxed with mechanical stirring. After 5 h the resulting thick suspension was cooled. Lutidinium bromide was filtered and lutidine evaporated at reduced pressure. The residue was taken up in ether, filtered through a short plug of silica gel to remove the most of the tarry materials. Evaporation of ether yielded a brown oil, which was fractionally distilled through a Vigreux column to give a colourless liquid. Yield 5.63 g (0.0249 mol, 24.9%). B.p. 112-114/0.1 torr, $n^{21}D$ 1.4754. IR(neat) 3040, 1730, 1705, 1595, 1430, 1190, 1160, 1020 cm^{-1}. ^{1}H-NMR(300 MHz) δ: 1.25 (t, 3H, OCH_2CH_3), 2.58 and 3.22 (AB, 1H each, J_{AB}=17 Hz, CH_2CO_2), 2.77 and 3.49 (ddd, 1H each, J=19, 3, 2 Hz, H-5), 3.70 (s, 3H, OCH_3), 4.14 (q, 2H, OCH_2CH_3), 6.19 (dt, 1H, J=6, 2 Hz, H-3), 7.84 (dt, 1H, J=6, 3 Hz, H-4). ^{13}C-NMR(75 MHz) δ: 14.0 (CH_3CH_2O), 38.4 (CH_2CO_2), 40.3 (C-5), 52.6 (OCH_3), 55.4 (C-1), 60.8 (CH_3CH_2O), 131.2 (C-3), 164.6 (C-4), 169.8 and 170.6 (CO esters), 203.6 (C-2). Anal. calcd. for $C_{11}H_{14}O_5$: C 58.40, H 6.24; found C 58.27, H 6.23.

Methyl 3-(1-methoxycarbonyl-2-oxocyclopent-3-en-1-yl)propionate (6b)

Dehydrobromination of methyl 3-(3-bromo-1-methoxycarbonyl-2-oxocyclopent-1-yl)propionate (prepared by the usual[13] bromination of the corresponding 2-oxocyclopentane diester[14]) was carried out in the same manner and at the same scale as described above. Yield 8.34 g (0.0369 mol, 36.9%). B.p. 116-120°C/0.1 torr, $n^{26}D$ 1.4820. IR(neat): 3040, 1730, 1705, 1600, 1430, 1195, 1170 cm^{-1}. ^{1}H-NMR(300 MHz) δ: 2.2-2.5 (m, 4H, $CH_2CH_2CO_2$), 2.62 and 3.26 (ddd, 1H each, J=19, 3, 2 Hz, H-5), 3.66 and 3.72 (s, 3H each, OCH_3), 6.19 (dt, 1H, J=6, 2 Hz, H-3), 7.79 (dt, 1H, J=6, 3 Hz, H-4). ^{13}C-NMR(75 MHz) δ: 29.2 and 29.3 ($CH_2CH_2CO_2$), 39.6 (C-5), 51.6 and 52.7 (OCH_3), 56.7 (C-1), 132.0 (C-3), 163.5 (C-4), 173.0 and 170.6 (CO esters), 204.8 (C-2). Anal. calcd. for $C_{11}H_{14}O_5$: C 58.40, H 6.24; found C 58.22, H 6.15.

Ethyl 1-Methoxycarbonyl-7-methyl-4-nitro-1-oxo-2,3,3a,4,5,6-hexahydroinden-2-ylacetate (7a)

To a stirred solution of **6a** (10 g, 44.2 mmol) and nitropentanone (5.79 g, 44.2 mmol) in 40 ml dry t-BuOH was added t-BuOK (0.5 g, 4.4 mmol) in 20 ml t-BuOH and the mixture was refluxed for 6 h under nitrogen. Then it was cooled, diluted with CH_2Cl_2 (50 ml) and washed succesively with 0.1 M HCl and satd. NaCl solutions. The aqueous washings were extracted twice with CH_2Cl_2 and the collected organic layers were dried over $MgSO_4$. The solvents were evaporated in vacuo and the residue was triturated with ice-cold ether. The precipitating crystals were filtered to give 3.85 g (11.3 mmol, 25.7%) of a single diastereomer of **7a**. m.p. 109-110°C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.23 (3H, t, CH_3-CH_2O) 1.77 (1H, dd, J=13, 11 Hz, H-3), 2. 18 (1H, m, H-5), 2.19 (3H, d, J=2.4 Hz, CH_3-7), 2.40 (1H, m, H-5), 2.52 (1H, m, H-6), 2.60 (1H, m, H-6), 2.83 (1H, m, H-3), 2.77 and 3.11 (2H overall, AB, J_{AB}=17.6 Hz, CH_2-2), 3.50 (1H, m, H-3a), 3.72 (3H, s, CH_3O), 4.10 (2H, q, CH_3-CH_2O), 4.31 (1H ddd, J=12.5, 10.5, 3.4 Hz, H-4). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ: 198.3 (C-1), 57.6 (C-2), 35.4 (C-3), 40.1 (C-3a), 86.8 (C-4), 27.0 (C-5), 32.9 (C-6), 150.4 (C-7), 128.0 (C-7a), 18.3 (CH_3-7), 169.8 and 170.3 (CO esters), 38.8 (CH_2-2), 60.6 (CH_3-CH_2O), 13.8 (CH_3-CH_2O). IR (KBr, cm^{-1}): 1735, 1705, 1640, 1555, 1380, 1215, 1180. MS(EI) m/z(%): 308 (M-31, 12.5), 294 (M-45, 45.3), 261 (11), 247 (17), 233 (38.4), 219 (11), 205 (16), 187 (30), 159 (33), 91 (25), 43 (100). MS(CI, NH_3) m/z(%): 357 (M+18, 100), 340 (82), 310 (11). Anal. calcd. for $C_{16}H_{21}O_7N$: C 56.63, H 6.24, N 4.13; found C 56.72, H 6.22, N 4.16.

The mother liquor was purified by column chromatography (eluent hexane-ethyl acetate (7:3)) to afford a semisolid mass (5.24 g, 15.47 mmol, 35%). ^{13}C-NMR spectrum showed that it contained two

diastereomers of **7a** in a ratio of 1:2.5. The signals of the major stereoisomer were identical with those of the crystalline one described above. Characteristic signals of the minor isomer: ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 2.73 and 3.02 (AB, J_{AB}=17 Hz, CH_2-2), 3.27 (m, H-3a), 4.39 (m, H-4). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ: 27.2 (C-5), 32.8 (C-6), 38.9 (C-3a), 86.7 (C-4), 150.7 (C-7), 127.7 (C-7a), 199.0 (C-1).

Methyl 3-(1-Methoxycarbonyl-7-methyl-4-nitro-1-oxo-2,3,3a,4,5,6-hexahydroinden-2-yl)propionate (7b)

Cyclization of nitropentanone (9.2 g, 70 mmol) and cyclopentenone diester **6b** (15.8 g, 70 mmol) was completed as described above. Column chromatography (eluent hexane-ether 1:4)) of the crude product afforded a pale yellow oil (15.5 g, 45.6 mmol, 65%), which was a 1:3.25 mixture of two diastereomers. ^{1}H-NMR (300 MHz, $CDCl_3$) major isomer δ: 1.50 (1H, dd, J=12.4, 12 Hz H-3), 1.85-2.78 (10H, m, CH_2), 2.20 (3H, d, J=2 Hz, CH_3-7), 3.65 and 3.72 (3H, s each, CH_3O), 3.28 (1H, m, H-3a), 4.35 (1H, ddd, J=12, 9, 4 Hz, H-4); minor isomer δ: 3.36 (m, H-3a), 4.24 (m, H-4). ^{13}C-NMR (72.5 MHz, $CDCl_3$) major isomer δ: 199.8 (C-1), 59.5 (C-2), 35.0 (C-3), 39.2 (C-3a), 86.6 (C-4), 27.3 (C-5) 33.1 (C-6), 150.9 (C-7), 127.3 (C-7a), 18.5 (CH_3-7), 173.2 and 171.4 (CO esters), 27.3 and 29.5 (CH_2-CH_2-CO_2), 51.7 and 52.6 (CH_3O); minor isomer δ: 27.0 (C-5), 40.2 (C-3a), 33.5 (C-6), 86.8 (C-4). IR (film, cm^{-1}): 1740, 1700, 1640, 1540, 1340, 1200, 1160. Anal. calcd. for $C_{16}H_{21}O_7N$: C 56.63, H 6.24, N 4.13; found C 56.75, H 6.29, N 4.10.

7-Methyl-4-nitro-2,3,3a,4,5,6-hexahydroinden-1-one (7c)

To a stirred solution of cyclopent-2-enone (0.82 g, 10 mmol) and nitropentanone (1.31 g, 10 mmol) in 10 ml dry t-BuOH was added t-BuOK (0.11 g, 1 mmol) in 5 ml t-BuOH and the mixture was heated at 60 °C for 4 h under nitrogen. Then it was cooled, diluted with ether (10 ml) and washed succesively with 0.1 M HCl and satd. NaCl solutions. The aqueous washings were extracted twice with ether and the collected organic layers were dried over $MgSO_4$. The solvents were evaporated in vacuo and the residue was dissolved in benzene (30 ml). The mixture was refluxed in the presence of p-toluenesulfonic acid (0.1 g) for 3.5 h while water being removed with Dean-Stark trap. Then it was washed with satd. NaCl solution, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (eluent hexan-ether (1:4)) to afford the crystalline *trans* isomer (0.99 g, 5 mmol, 50%) and the *cis* isomer (0.17 g, 0.798 mmol, 7.98%) as a yellow oil.

trans-**7c**: R_f=0.73 (hexan-ether (1:4)). m.p. 87-88°C (lit.[5] m.p. 87-88). IR(KBr, cm^{-1}): 1705, 1635, 1539, 1372. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.60 (1H, m), 2.17 (3H, d, J=2.5 Hz, CH_3-7), 2.0-2.6 (7H, m), 3.20 (1H, m), 4.32 (1H, td, J=11, 4 Hz, H-4). ^{13}C-NMR (25 MHz, $CDCl_3$) δ: 204.9 (C-1), 38.0 (C-2), 25.7 (C-3), 42.9 (C-3a), 87.2 (C-4), 27.5 (C-5), 32.9 (C-6), 146.7 (C-7), 129.0 (C-7a). MS(EI) m/z(%): 195 (3.4, M^+), 149 (24), 148 (100), 107 (19), 106 (15), 105 (30), 91 (29), 79 (15), 77 (17).

cis-**7c**: R_f=0.44 (hexan-ether (1:4)). IR(film, cm^{-1}): 1700, 1630, 1540, 1360. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.60 (1H, m), 2.19 (3H, d, J=2.5 Hz, CH_3-7), 1.90-2.70 (7H, m), 3.04 (1H, m), 5.10 (1H, m, H-4). ^{13}C-NMR (25 MHz, $CDCl_3$) δ: 204.6 (C-1), 38.0 (C-2), 23.0 (C-3), 40.7 (C-3a), 81.5 (C-4), 25.5 (C-5), 29.4 (C-6), 147.9 (C-7), 126.9 (C-7a). The *cis* diastereomer (120 mg) was converted to the *trans* isomer upon treatment with t-BuOK (50 mg) in refluxing t-BuOH (2 ml).

Nef Reaction of Bicyclic Nitro Compounds 7a,b. General Procedure.

A solution of **7a,b** (25 mmol) in THF (50 ml) was treated with sodium methoxide (prepared on dissolution of 0.6 g (25 mmol) sodium in 50 ml methanol) at 15°C under nitrogen. To the sodium nitronate thus formed was quickly added a buffered solution of titanium(III)-chloride (prepared by mixing 140 ml 15 w/w% (ca. 0.1 mol) $TiCl_3$ and aq. solution of ammonium acetate (47 g, 0.61 mol in 140 ml water)). The resulting dark solution was stirred for an hour at room temperature and then extracted thoroughly with ether. The collected etheral phases were washed with satd. $NaHCO_3$ and NaCl solutions and dried over $MgSO_4$. Evaporation of the solvents and azeotropic distillation of acetic acid with benzene yielded an oil

which was pure according to TLC test (hexane-ether (1:9)). It was used without further purification in the next step.

Ethyl 1-Methoxycarbonyl-7-methyl-1,4-dioxo-2,3,3a,4,5,6-hexahydroinden-2-ylacetate (**8a**)

Yield 81.5%. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.22 (3H, t, CH_3-CH_2O), 2.0 (1H, dd, J=14.3, 12.8 Hz, H-3), 2.10-3.0 (6H, m), 2.33 (3H, d, J=2.5 Hz, CH_3-7), 2.69 and 3.20 (2H overall, AB J_{AB}=17 Hz, CH_2-2), 3.72 (3H, s, CH_3O), 4.10 (2H, q, CH_3-CH_2O). ^{13}C-NMR (25 MHz, $CDCl_3$) δ: 198.4 (C-1), 58.9 (C-2), 35.1, 31.6, 33.7 (C-3, C-5, C-6 interchangable), 47.6 (C-3a), 209.4 (C-4), 152.4 (C-7), 128.6 (C-7a), 19.1 (CH_3-7), 169.9 and 170.7 (CO esters), 39.2 (CH_2-CO_2), 60.7 (CH_3-CH_2O), 14.0 (CH_3-CH_2O), 52.7 (OCH_3). IR (film, cm^{-1}): 1730, 1710, 1705, 1640, 1150-1190.

Methyl 3-(1-Methoxycarbonyl-7-methyl-1,4-dioxo-2,3,3a,4,5,6-hexahydroinden-2-yl)propionate (**8b**)

Yield 97%. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.85 (1H, m, H-3), 2.28 (3H, d, J=2.5 Hz, CH_3-7), 2.0-2.70 (9H, m), 2.85 (1H, m, H-3a), 3.62 and 3.71 (s, 3H each, CH_3O). ^{13}C-NMR (25 MHz, $CDCl_3$, major isomer only) δ: 199.0 (C-1), 60.4 (C-2), 29.5, 30.9, 33.7, 35.1 (CH_2, two overlapping peaks), 47.1 (C-3a), 151.9 (C-7), 128.7 (C-7a), 18.8 (CH_3-7), 172.7 and 171.4 (CO esters), 52.3 and 51.3 (CH_3O). IR (film, cm^{-1}): 1740, 1715, 1700, 1640, 1430, 1370, 1170-1205.

4-Hydroxy-7-methyl-1-oxoindan-2-ylacetic acid (4a)

Enedione **8a** (6.16 g, 20 mmol) was dissolved in ethanol (70 ml) and $Ba(OH)_2.8H_2O$ (28 g, 88 mmol) suspended in water (200 ml) was added. The mixture turned brownish red instantaneously and was refluxed for 5 h. The progress of the reaction was monitored by TLC (benzene-methanol (4:1)). Then it was cooled, acidified with cc. HCl and extracted with ethyl acetate. The collected oganic phases were dried over $MgSO_4$ and then concentrated. The residue was crystallized from cold benzene and the mother liquor was purified by column chromatography (eluent benzene-ethyl acetate-methanol (8:2:1)). Yield 2.2 g (10 mmol, 50%). m.p 206-208°C (lit.[10] m.p. 208-211). ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 2.54 and 2.61 (1H each, dd, J=17, 4 Hz, CH_2-2), 2.71 (1H, dd, J=17, 4 Hz, H-3), 2.83 (1H, ddd, J=8, 4, 4 Hz, H-2), 3.18 (1H, dd, J=17, 8 Hz, H-3), 6.92 and 6.97 (1H each, AB, J_{AB}=8 Hz, H-5 and H-6). ^{13}C-NMR (25 MHz, DMSO-d_6) δ: 207.6 (C-1), 43.5 (C-2), 28.9 (C-3), 152.6 (C-4), 119.7 (C-5), 130.0 (C-6), 134.6 (C-7), 140.5 (C-7a), 127.3 (C-3a), 16.9 (CH_3-7), 34.7 (CH_2-2), 173.1 (CO_2). MS(EI) m/z(%): 220 (M^+, 50), 202 (22), 175 (50), 174 (48), 172 (50), 160 (100), 145 (20), 131 (15), 115 (8). IR (KBr, cm^{-1}): 3240, 3020, 1720, 1680, 1600, 1505, 1290, 1250, 1170. Anal. calcd. for $C_{12}H_{12}O_4$: C 65.45, H 5.49; found C 65.64, H 5.35.

3-(4-Hydroxy-7-methyl-1-oxoindan-2-yl)propionic acid (4b)

Enedione **8b** (20 mmol) was transformed to **4b** using the same procedure as above. Yield 47%. m.p. 194-195°C. ^{1}H-NMR (250 MHz, DMSO-d_6) δ: 1.60 (1H, m), 2.02 (1H, m), 2.24-2.39 (2H, m), 2.42 (3H, s, CH_3-7), 2.57 (2H, m), 3.12 (1H, dd, J=16, 7 Hz, H-3), 6.92 and 6.96 (1H each, AB, J_{AB}=8 Hz, H-5 and H-6). ^{13}C-NMR (25 MHz, DMSO-d_6) δ: 208.8 (C-1), 46.3 (C-2), 28.6 (C-3), 152.7 (C-4), 119.8 (C-5), 130.1 (C-6), 134.6 (C-7), 140.6 (C-7a), 127.4 (C-3a), 17.0 (CH_3-7), 26.4 (CH_2-2), 31.6 (CH_2-CO_2), 174.2 (CO_2). MS(EI) m/z(%): 234 (M^+, 61), 216 (M-18, 35), 175 (46), 161 (100), 145 (31, 91 (23). IR (KBr, cm^{-1}): 3176, 3025, 1705, 1676, 1594, 1508, 1434, 1288, 1231, 1163, 920, 825. Anal. calcd. for $C_{13}H_{14}O_4$: C 66.66, H 6.02; found C 66.50, H 5.91.

7-methyl-1,4-dioxo-2,3,4,5,6,7-hexahydroinden-2-ylacetic acid (3a)

Enedione **8a** (1.66 g, 5.38 mmol) in DME (30 ml) and 5% aq. H_2SO_4 (30 ml) was refluxed for 72 h under nitrogen. Then the mixture was diluted with water (50 ml) and extracted with $CHCl_3$ (5x30 ml). The collected organic layers were dried over $MgSO_4$, concentrated and the residue was purified by column chromatography (eluent benzene-ethyl acetate-methanol (8:2:1)). From the pure fractions a 1:1 diastereomeric mixture of the diketo acid **3a** was isolated, which crystallized on trituration with cold ether. Yield 0.74 g (3.34 mmol, 62%). m.p. 141-142°C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.27 and 1.23 (3H overall, 2xd, J=3Hz, CH_3-7), 1.90 (1H, m), 2.24 (1H, m), 2.32-2.90 (7H, m), 2.98 (1H, m). 9.76 (1H,

broad s, CO_2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$, one diastereomer only) δ: 17.0 (CH_3-7), 26.5 (C-7), 29.6 (C-5), 30.4 (C-6), 34.8, 36.0 (C-3, CH_2-2 interchangable), 42.5 (C-2), 156.5 (C-7a), 157.2 (C-3a), 176.6 (CO_2), 199.2 (C-4), 209.7 (C-1). MS(EI) m/z(%): 222 (M^+, 50), 204 (91), 176 (60), 161 (44), 148 (100), 133 (75), 121 (52), 105 (57), 91 (98), 79 (45). IR (KBr, cm^{-1}): 3200-3140, 1730, 1690, 1680, 1640, 1205, 1180. Anal. calcd. for $C_{12}H_{14}O_4$: C 64.85, H 6.35; found C 64.98, H 6.27.

3-(7-Methyl-1,4-dioxo-2,3,4,5,6,7-hexahydroinden-2-yl)-propionic acid (3b)

Enedione **8b** (1.2 g, 3.89 mmol) was hydrolyzed and decarboxylated as described for **3a**. Column chromatography allowed one to isolate a 1:1 diastereomeric mixture of the diketo acid **3b** as a pale yellow semisolid mass. Yield 0.53 g (2.24 mmol, 57.7%). ^{1}H-NMR (80 MHz, $CDCl_3$) δ: 1.20 (3H, d, CH_3-7), 1.40-3.0 (12H, m), 9.30 (1H, broad s, CO_2H). ^{13}C-NMR (25 MHz, $CDCl_3$, one diastereomer only) δ: 16.9 (CH_3-7), 26.0 (CH_2-2), 26.4 (C-7), 29.5 (CH_2-CO_2), 30.4, 31.4 (C-5, C-6 interchangable), 35.7 (C-3), 45.2 (C-2), 156.4 and 157.0 (C-7a and C-3a), 177.5 (CO_2), 199.0 (C-4), 210.8 (C-1). IR (film, cm^{-1}): 3400-3300, 1720, 1690, 1660, 1420, 1200-1140. MS(EI) m/z(%): 236 (54, M^+), 219 (100), 203 (70), 164(35), 149 (26), 91 (37), 55 (53), 45 (49).

Formation of the Ethylene Ketal of 8a,b. General Procedure.

A mixture of enedione **8a,b** (10 mmol) and ethylene glycol (3.1 g, 50 mmol) was refluxed in benzene (100 ml) in the presence of p-TsOH (0.2 g) under nitrogen with continuous removal of water via a Dean-Stark apparatus. After an hour TLC analysis (hexane-ether (1:9)) showed the completion of the reaction. Then the mixture was washed with satd. $NaHCO_3$ and NaCl solutions. Drying over $MgSO_4$ was followed by the evaporation of the solvent and the residue was purified by column chromatography (eluent hexane-ether (1:9)).

Ethyl 4,4-Ethylenedioxy-2-methoxycarbonyl-7-methyl-1-oxo-2,3,3a,4,5,6-hexahydroinden-2-ylacetate (**9a**)

Yield 70%. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.23 (3H, t, CH_3-CH_2O), 1.82 (2H, m), 2.18 (3H, d, CH_3-7), 2.44 (1H, m), 2.53 and 3.21 (2H overall, AB, J_{AB}=16 Hz, CH_2-2), 2.68 (1H, dd, J=12, 8 Hz) 3.68 (3H, s, CH_3-O) 4.02 (4H, m, O-$(CH_2)_2$-O), 4.12 (q, 3H, CH_3-CH_2O). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ: 198.9 (C-1), 58.3 (C-2), 43.3 (C-3a), 107.9 (C-4), 151.3 (C-7), 129.5 (C-7a), 18.5 (CH_3-7), 170.8 and 170.5 (CO esters), 30.8, 31.0, 33.5 and 39.8 (C-3, C-5, C-6, CH_2-2 interchangable), 65.4, 64.7 (O-$(CH_2)_2$-O). IR (film, cm^{-1}): 1740, 1705, 1640, 1425, 1205-1160, 1020, 940.

Methyl 3-(4,4-Ethylenedioxy-2-methoxycarbonyl-7-methyl-1-oxo-2,3,3a,4,5,6-hexahydroinden-2-yl)propionate (**9b**)

Yield 68%. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.6-2.05 (4H, m), 2.15 (3H, d, J=2.5 Hz, CH_3-7), 2.22-2.50 (6H, m), 3.15 and 3.03 (1H overall, m, H-3a), 3.65 and 3.69 (3H, s each, CH_3O), 4.0-4.05 (4H, m, O-$(CH_2)_2$-O). ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ: 200.4 (C-1), 59.3 (C-2), 43.0 (C-3a), 107.5 (C-4), 150.8 (C-7), 129.5 (C-7a), 18.3 (CH_3-7), 170.1 and 173.0 (CO esters), 52.3 and 51.3 (CH_3O), 29.4, 29.7, 29.8, 30.8, 33.4 (C-3, C-5, C-6, CH_2-2, CH_2-CO_2 interchangable), 64.6, 65.3 (O-$(CH_2)_2$-O). IR (film, cm^{-1}): 1740, 1715, 1700, 1640, 1430, 1370, 1170-1205.

Conjugate Addition of $LiMe_2Cu$ to 9a,b. General Procedure.

In a flame-dried three-necked flask equipped with a dropping funnel, a nitrogen inlet and a rubber septum copper(I)-iodide (1.07 g, 5.62 mmol) was suspended in dry ether (25 ml) under nitrogen. The flask was cooled with salt-ice bath to ca. -10°C and methyl lithium (1.3 M, 11.25 mmol, 8.6 ml) was introduced by syringe with vigorous agitation. To the resulting straw-yellow solution **9a,b** (3.12 mmol) was added dropwise over 15 min. Stirring was continued in the cold for 1 h. Then the mixture was poured into satd. NH_4Cl solution (50 ml) and the two phases were separated. The aqueous layer was extracted with ether and the collected etheral phases were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (eluent hexane-ether (1:3)).

*Ethyl 7,7-Dimethyl-4,4-Ethylenedioxy-2-methoxycarbonyl-1-oxo-perhydroinden-2-ylacetate (**10a**)*

Yield 47.8%. m.p. 121-122°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.92, 1.25 (6H overall, s each, CH_3-7), 1.25 (3H, t, OCH_2-CH_3), 1.20-1.70 (4H, m), 1.79 (1H, dd, J=12.4, 11.6 Hz, H_{ax}-3), 2.26 (1H, d, J=14 Hz, H_{ax}-7a), 2.40-2.65 (2H, m), 2.69 and 3.03 (1H each, AB, J_{AB}=17.1 Hz), 3.68 (3H, s, CH_3O), 3.97 (4H, m, O-$(CH_2)_2$-O), 4.13 (2H, q, OCH_2-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 18.7, 28.4 (CH_3-7), 13.9 (CH_3-CH_2O), 30.6 32.1 (C-5, C-6 interchangable), 32.2 (C-7), 39.3, 39.4 (C-3, CH_2-2), 41.7 (C-3a), 52.4 (CH_3O), 57.6 (C-2), 59.1 (C-7a), 60.6 (CH_3-CH_2O), 65.0, 65.2 ($O(CH_2)_2O$), 109.7 (C-4), 170.6, 170.3 (CO esters), 210.5 (C-1). IR (KBr, cm^{-1}): 1750, 1730, 1440, 1210, 1180, 940. Anal. calcd. for $C_{19}H_{28}O_7$: C 61.94 H 7.66 found C 61.74, H 7.55.

*Methyl 3-(7,7-Dimethyl-4,4-Ethylenedioxy-2-methoxycarbonyl-1-oxo-perhydroinden-2-yl)propionate (**10b**)*

Yield 43%. m.p. 92-94.5°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 and 1.22 (3H, s each, CH_3-7), 1.30-2.60 (12H, m), 3.66, 3.71 (3H, s each, CH_3O), 3.98-4.02 (4H, m, $O(CH_2)_2O$). ^{13}C-NMR (100 MHz, $CDCl_3$, major isomer only) δ: 18.7 and 28.4 (CH_3-7), 29.5, 30.5, 32.0, (C-5, C-6, $CH_2CH_2CO_2$ interchangable), 32.1 (C-7), 39.3 (C-3), 41.5 (C-3a), 51.5, 52.3 (CH_3O), 58.9 (C-2), 59.2 (C-7a), 65.1, 65.2 (OCH_2CH_2O), 109.6 (C-4), 171.3, 173.2 (CO esters), 211.2 (C-1). IR (KBr, cm^{-1}): 1730, 145, 1195, 1160, 940. Anal. calcd. for $C_{19}H_{28}O_7$: C 61.94 H 7.66 found C 61.69, H 7.55.

Oxydative Hydrolysis and Decarboxylation of 10a,b. General Procedure.

Keto diester **10a,b** (1 mmol) was refluxed in acetic acid (4.5 ml) and 6 M HCl (4.5 ml) under oxygen atmosphere. After 5 h TLC analysis (benzene-methanol (4:1)) showed the disappearance of the starting material and a single product. Then the mixture was diluted with water (10 ml) and extracted thoroughly with ethyl acetate. The collected organic phases were dried oer $MgSO_4$ and concentrated. Traces of acetic acid were removed by azeotropic distillation with benzene. The residue was purified by column chromatography (eluent benzene-methanol (10:1)).

*7,7-Dimethyl-1,4-dioxo-2,3,4,5,6,7-hexahydroinden-2-ylacetic acid (**2a**)*

Yield 65%. m.p. 133.5-134°C (lit[5] m.p. 136-138°C). ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.30, 1.32 (6H overall, s each, CH_3-7), 1.32 (1H, dd, J= 18, 3 Hz), 1.92 (2H, t, J=7 Hz), 2.58 (2H, dd, J=13, 7 Hz), 2.68 (2H, m), 2.75-3.05 (2H, m), 10.15 (1H, broad s, CO_2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ: 24.8, 25.2 (CH_3-7), 29.1, 35.2, 34.4, 38.1 (CH_2), 32.0 (C-7), 42.0 (C-2), 156.1 (C-7a), 158.2 (C-3a), 176.8 (CO_2), 199.3 (C-4), 209.4 (C-1). IR (KBr, cm^{-1}): 3200-3160, 1730, 1695, 1660, 1200, 1150.

*3-(7,7-Dimethyl-1,4-dioxo-2,3,4,5,6,7-hexahydroinden-2-yl)propionic acid (**2b**)*

Yield 57.1%. m.p. 101°C. ^{1}H-NMR (250 MHz, $CDCl_3$) δ: 1.31, 1.32 (6H over all, s each, CH_3-7), 1.73 (1H, m), 1.91 (2H, t, J=7Hz, H-6), 2.10 (1H, m), 2.25 (1H, dd, J=18, 3 Hz, H-3), 2.49 (1H, m), 2.51 (2H, t, J=7 Hz, H-5), 2.57 (2H, t, J=7 Hz), 2.87 (1H, dd, J=18, 3 Hz, H-3). ^{13}C-NMR (25 MHz, $CDCl_3$) δ: 25.3 (CH_3-7), 26.3 (CH_2-2), 29.2, 31.4, (C-5, C-6), 32.3 (C-7), 35.4 (C-3) 38.2 (CH_2-CO_2), 45.5 (C-2), 156.6 (C-7a), 158.3 (C-3a), 177.8 (CO_2), 199.1 (C-4), 210.8 (C-1). IR (KBr, cm^{-1}): 3388-3056, 1710, 1694, 1678, 1427, 1286, 1231, 1160, 972, 910, 870. Anal. calcd. for $C_{14}H_{18}O_4$: C 67.18, H 7.25; found C 67.30, H 7.19.

***cis*-5-Hydroxy-3,3a,4,8b-tetrahydroindeno[1,2-b]furan-2-one (12a)**

Indanone **4a** (0.24 g, 1.1 mmol) was dissolved in 1 M NaOH solution (5 ml) and treated with $NaBH_4$ (0.08 g, 2.2 mmol) in several portions. The mixture was stirred for two days at room temperature and the reaction was monitored by TLC (benzene-methanol (4:1)). Then the solution was cooled with an ice-bath and carefully acidified with dil. HCl. Stirring was continued for 2 h and lactone **12a** was isolated by extration with ethyl acetate. Crystallization from cold ether yielded 0.19 g (0.93 mmol, 84%) of white crystals. m.p. 144-145°C. (lit.[10] m.p. 145-146°C) ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 2.23 (3H, s, CH_3-8), 2.42 (1H, dd, J=18, 4 Hz, H-3), 2.67 (1H, dd, J=16, 4 Hz, H-4), 2.93 (1H, dd, J=18, 10 Hz, H-3), 3.13 (1H, dd, J=16, 9 Hz, H-4), 3.28 (1H, m, H-3a), 5.90 (1H, d, J=7 Hz, H-8b), 6.70 (1H, d, J=7 Hz, H-6),

6.90 (1H, d, J=7 Hz, H-7), 9.28 (1H, s, OH). ^{13}C-NMR (75 MHz, DMSO-d_6) δ: 87.1 (C-8b), 35.4 (C-3), 36.2 (C-3a), 35.2 (C-4), 151.8 (C-5), 115.8 (C-6), 129.2 (C-7), 129.4 (C-8), 139.2 (C-8a), 125.5 (C-4a), 17.2 (CH_3-8), 177.1 (C-2). MS(EI) m/z(%): 204 (M^+, 47), 159 (16), 145 (100), 115 (19), 91 (18). IR (KBr, cm^{-1}): 3248, 3027, 1728, 1725, 1600, 1500, 1300, 1262, 1200, 1168, 800.

***trans*-3-(1,4-Dihydroxy-7-methylindan-2-yl)propionic acid (11b)**

Indanone **4b** (0.7 g, 3 mmol) was dissolved in 1 M NaOH solution (25 ml) and treated with $NaBH_4$ (0.2 g, 5.3 mmol) in several portions. After two days, solution was carefully acidified to pH 3-4 with dil. HCl and quickly extracted with ethyl acetate (4x20 ml). The collected organic phases were dried over $MgSO_4$ and concentrated to afford 0.7 g (2.96 mmol, 98.8%) dihydroxy acid. m.p.137-139°C. ^{1}H-NMR (250 MHz, DMSO-d_6) δ: 1.55, 1.79 (2H overall, m each, CH_2-2), 2.0-2.20 (2H, m), 2.21 (3H, s, CH_3-7), 2.36 (2H, t, J=8 Hz, CH_2-CO_2), 2.97 (1H, dd, J=16, 8 Hz, H-3), 4.67 (1H, d, J=5 Hz, H-1), 6.52 (1H, d, J=8Hz, H-5), 6.72 (1H, d, J=8Hz, H-6), 8.9 (1H, s, OH). ^{13}C-NMR (62.5 MHz, DMSO-d_6) δ: 79.9 (C-1), 48.1 (C-2), 28.9, 32.1 and 32.7 (C-3, and $CH_2CH_2CO_2$), 151.2 (C-4), 113.8 (C-5), 128.6 (C-6), 144.5 (C-7), 127.6 (C-7a), 124.9 (C-3a), 17.3 (CH_3-7), 174.8 (CO_2). MS(EI) m/z(%): identical with that of the δ-lactone **12b**. IR (film, cm^{-1}): 3521, 3408, 3137, 3020, 1710, 1600, 1490, 1404, 1270, 1239, 1019, 800. Anal. calcd. for $C_{13}H_{16}O_4$: C 66.09, H 6.83; found C 65.95, H 6.79.

***cis*-6-Hydroxy-9-methyl-3,4,4a,5,9b-tetrahydroindeno[1,2-b]pyran-2-one (12b)**

Indanone **4b** (0.8 g, 3.42 mmol) was reduced with $NaBH_4$ (0.25 g, 6.84 mmol) in 1 M NaOH solution as described above. After two days, the pH of the solution was adjusted to 1 with dil. HCl and stirring was continued for 10 h. Then the mixture was extracted with ethyl acetate and the organic phase was dried over $MgSO_4$. Evaporation of the solvent gave the mixture of lactone **12b** and *trans*-**11b**, and a trace of *cis*-**11b** according to TLC analysis (benzene-methanol (4:1)) and confirmed by the examination of the NMR spectra. Separation was carried out by column chromatography (eluent benzene-methanol (5:1)). The pure fractions afforded the *trans*-hydroxy acid **11b** (170 mg, 0.72 mmol, 21%) and the *cis*-δ-lactone **12b** (230 mg, 0.97 mmol, 28.5%). m.p. 165-167°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.81 (1H, m, H-4), 2.28 (1H, m, H-4), 2.32 (3H, s, CH_3-9), 2.43 (2H, t, J=6 Hz, H-3), 2.74 (1H, dd, J=16, 7 Hz, H-5), 2.90 (1H, m, H-4a), 3.18 (1H, dd, J=16, 8 Hz, H-5), 5.77 (1H, d, J=7.5 Hz, H-9b), 6.71 (1H, d, J=8 Hz, H-7), 6.89 (1H, d, J=8 Hz, H-8), 7.52 (broad s, OH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 17.6 (CH_3-8), 24.2 (C-4), 28.5 (C-3), 34.2 (C-5), 34.9 (C-4a), 84.5 (C-9b), 116.1 (C-7), 127.3 (C-5a), 129.3 (C-9a), 129.6 (C-8), 139.5 (C-9), 150.7 (C-6), 173.2 (C-2). MS(EI) m/z(%): 218 (M^+, 64), 159 (23), 158 (31), 146 (55), 145 (100), 131 (25), 115 (16), 91 (14). IR (KBr, cm^{-1}): 3240, 3010, 1700, 1600, 1500, 1460, 1250, 1180, 980, 800. Anal. calcd. for $C_{13}H_{14}O_3$: C 71.54, H 6.47; found C 71.61, H 6.55.

Acknowledgments

This work was financially supported by the National Fund for Science and Research (OTKA Poject No. 5-355 and 5-349). Grant from József Varga Foundation provided to G. Árvai is gratefully appreciated.

REFERENCES

1. (a) Cook, C.E.; Whichard, L.P.; Wall, M.E.; Egley, G.H.; Coggon, P.; Luhan, P.A.; McPhail, A.T. *J. Am. Chem. Soc.* **1972**, *94*, 6198-6199. (b) Cook, C.E.; Whichard, L.P.; Turner, B; Wall, M.E.; Egley, G.H. *Science* **1966**, *154*, 1189-1190.
2. Pepperman, A.B.; Connick, W.J.; Vail, S.L.; Worsham, A.D.; Pavlista, A.D; Moreland, D.E. *Weed Sci.* **1982**, 561-566.

3. (a) Heather, J.B; Mittal, R.S.D.; Sih, J.C. *J. Am. Chem. Soc.* **1974**, *96*, 1976-1977. (b) Dolby, L.I; Hanson, G. *J. Org. Chem.* **1976**, *41*, 563-564. (c) Brooks, D.W.; Bevinakatti, H.S.; Kennedy, E.; Hathaway, J. *J. Org. Chem.* **1985**, *50*, 628-632.
4. Heather, J.B; Mittal, R.S.D.; Sih, J.C. *J. Am. Chem. Soc.* **1976**, *98*, 3661-6169.
5. McAlpine, G.A.;Raphael, R.A.; Shaw, A.; Taylor, A.W.; Wild, H *J. Chem. Soc. Perkin Trans.* **1976**, *1*, 410-416.
6. Raphael, R.A.; Telfer, S.J. *Tetrahedron Letters* **1985**, *26*, 489-492.
7. McMurry, J.E.; Melton, J. *J. Org. Chem.* **1973**, *38*, 4367-4373.
8. Miller, R.B.; Nash, R.D. *Tetrahedron* **1974**, *30*, 2961-2965.
9 House, H.O.; Babad, H.; Toothill, R.B.; Noltes, A.W. *J. Org. Chem.* **1962**, *27*, 4141-4146.
10. Kendall, P.M.; Johnson, J.V.; Cook, C.E. *J. Org. Chem.* **1979**, *44*, 1421-1424.
11. (a) Dauben, W.C.; Fonken, G.J.; Noyce, D.S. *J. Am. Chem. Soc.* **1956**, *78*, 2579-2582. (b) Wigfield, D.C. *Tetrahedron*, **1979**, *35*, 449-462.
12. Clark, J.H.; Cork, D.G. *Chem. Lett.* **1983**, 1145-1148.
13. Ravid, U.; Hoffer D.; Ikan. R. *Isr. J. Chem.* **1975**, *11*, 63-67.
14. Feutrill, G.I.; Mirrington, R.N. *J.Hetercycl. Chem.* **1978**, *13*, 693-694.

(*Received in UK* 2 *November* 1993; *revised* 8 *December* 1993; *accepted* 10 *December* 1993)