*Tetrahedron* Vol. 47, No 35, pp 7403-7408, 1991
Printed in Great Britain

0040-4020/91 $3 00+ 00


# Regiocontrol By The Carbon-Carbon Double Bond In The $Rh_2(OAc)_4$ Mediated Carbon-Hydrogen Insertion Of α-Diazo-Ketones.

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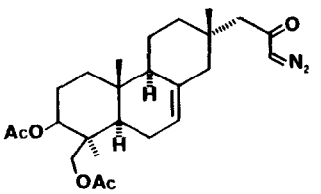
(*Received in UK 30 May* 1991)

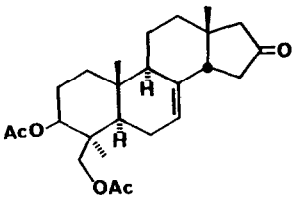
*Key Words*
Cyclic unsaturated α-Diazo ketones, Dirhodium tetraacetate, Carbon-hydrogen insertion, Cyclopropanation, Selectivity

**Abstract:** Diazo carbonyl compounds, when catalyzed by dirhodium tetraacetate, insert to allylic position This phenomenon was exploited in cyclic systems **3d**, **5d**, **5g**, and **10** The reactivity toward allylic insertion is corroborated by the unexpected six-membered ring cyclization in the transformation **5g** →**9**

Intramolecular carbon-carbon bond formation through metal-catalyzed reaction of α-diazo-ketones, constitutes a general method of cycloalkanones synthesis [1] Dirhodium tetracetate is a very efficient catalyst for these processes and leads mainly to cyclopentanones by carbon-hydrogen bond insertion [2] The reactivity of diazo-ketones bearing a remote carbon-carbon double bond in cyclic systems is illustrated by the transformation of diazopimarenone **1** into the compound **2** The regio- and diastereo- selectivity of this conversion was ascribed to the double bond participation in the quasi-axial allylic hydrogen bond rupture [2a]




**1**



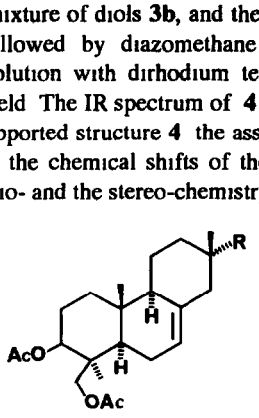

**2**

After this primary observation it was reported that in the decomposition of acyclic unsaturated diazo-ketones, the carbon-hydrogen bond insertion occurs to a greater extent than the cyclopropanation process and the electron withdrawing groups (e g vinyl, phenyl,[2e]) reduce the reactivity of the allylic carbon-hydrogen bond when compared with the aliphatic one [3]

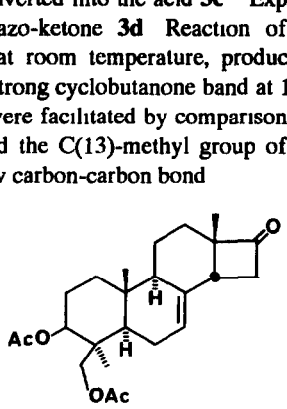
The different behaviour of cyclic and acyclic unsaturated diazo-ketones prompted us to prepare several cyclic models in order to obtain more information on the selectivity of the cyclization process

Diazo-ketone **3d** was prepared to test the influence of the diazocarbonyl chain length on the selectivity of the intramolecular insertion process versus **1** The treatment of virescenol B diacetate **3a**with osmium

tetroxide led to a mixture of diols **3b**, and there were converted into the acid **3c** [4] Exposure of the latter to oxalyl chloride followed by diazomethane led to diazo-ketone **3d** Reaction of this compound in dichloromethane solution with dirhodium tetraacetate, at room temperature, produced the D-norsteroid system **4** in 53% yield The IR spectrum of **4** showed a strong cyclobutanone band at 1780 $cm^{-1}$ The 13C NMR data fully supported structure **4** the assignments were facilitated by comparison of the values with those of **2** and **3a**, the chemical shifts of the C(11) and the C(13)-methyl group of **4** were essential in determining the regio- and the stereo-chemistry of the new carbon-carbon bond

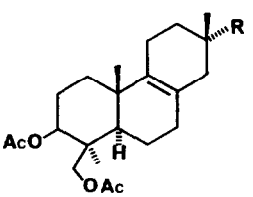



**3a**, R = $C_2H_3$
**b**, R = $CHOHCH_2OH$
**c**, R = $CO_2H$
**d**, R = $COCHN_2$

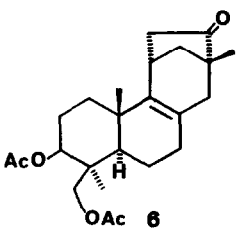



**4**

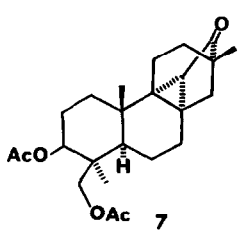
To explore the effect of the carbon-carbon double bond position, the compounds **5d** and **5g** were prepared Diazo-ketone **5d** was obtained starting from iso-virescenol B diacetate **5a**,[5] following the procedure described for **3d** Dirhodium tetraacetate-mediated reaction of **5d** afforded **6** and **7** in 21% and 52% yields respectively The $^{13}C$ NMR spectrum of **7** supported the presence of a cyclopropane system by the observation of five quaternary aliphatic carbon signals Significant heteronuclear long-range coupling correlation obtained from COLOC[6] allowed carbon assignments to be made The IR absorption at 1740 $cm^{-1}$ of **6** was consistent with a cyclopentanone moiety, and the $^{13}C$ NMR values suggested that the new carbon-carbon bond resides between C(11) and C(15) A comparison of the chemical shift values and multiplicities of **5a** and **6**, indicated that the C(11) methylene carbon in **5a** ($\delta$ 19 1) had been replaced by a methine carbon ($\delta$ 30 4) The $^{13}C$-$^{1}H$ shift correlated spectra allowed the detection of the resonance of the methine proton at the cyclization site ($\delta$ 2 76) NOE difference experiments revealed a close proximity of the C-10 methyl group ($\delta$ 1 03) and the methine proton at $\delta$ 2 76, thus confirming structure **6**




**5a**, R = $C_2H_3$
**b**, R = $CHOHCH_2OH$
**c**, R = $CO_2H$
**d**, R = $COCHN_2$

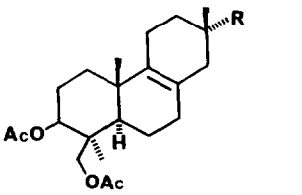



**6**

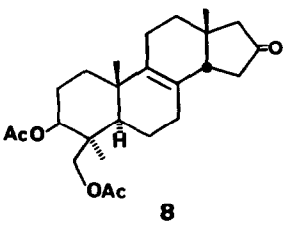



**7**

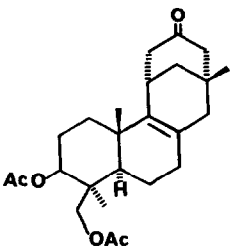
We next prepared the homoderivative **5g** following the procedure described for **1** [2a] Exposure of diazo-ketone **5g** to dirhodium tetraacetate led to ketones **8** and **9**, in 40% and 27% yield respectively [8] The structure of compound **8** was determined by a comparison of the spectroscopic data with those of compound **2** [2a] The $^{1}H$ NMR and $^{13}C$ NMR spectra of **9** showed a close resemblance to that of the cyclopentanone derivative **7** The methine proton at the cyclization site ($\delta$ 2 81), evidenced by $^{13}C$-$^{1}H$ shift correlated spectra, exhibited a strong NOE upon irradiation of the C-10 methyl resonance The presence of a cyclohexanone moiety in **9** was also unequivocally supported by the $^{13}C$ NMR carbonyl signal at 211 1 ppm [7] Formation of **9** involves an unexpected six membered ring annulation process To our knowledge, regiocontrol in the cyclohexanones forming reactions, by carbon-hydrogen insertion of carbenoids, was set up only with the presence of an activating neighbouring hydroxy group [9,10]




**5a**, R = $C_2H_3$
**e**, R = $CH_2CH_2OH$
**f**, R = $CH_2CO_2H$
**g**, R = $CH_2COCHN_2$



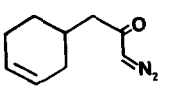

**8**



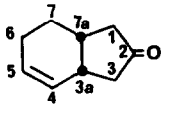

**9**

In summary we have explored the reactivity of unsaturated $\alpha$-diazo-ketones bearing a carbon-carbon double bond in cyclic systems In these compounds the $\alpha$-diazocarbonyl chain could interact with allylic and non allylic methylenes The observed regioselectivity seems to bee the proof of the influence of the carbon-carbon double bond in directing the carbon-hydrogen insertion

Since the systems being examined are highly rigid skeletons, the conclusions based on the stereoelectronic influences of cyclic double bonds could be compromised by steric and conformational effects Consequently we turned our attention to the reactivity of the simplest diazo-ketone **10**, prepared from 3-cyclohexen-1-acetic acid [11] Dirhodium tetraacetate catalyzed decomposition of **10** afforded *cis*-1,3,3a,6,7,7a-hexahydro-2H-inden-2-one **11** [12] as the only reaction product




**10**




**11**

A comparison of the carbon shifts of the *cis* ($\delta$ C-3a 39 9 ppm) and *trans*-hydrindane ($\delta$ C-3a 47 3 ppm), *cis* ($\delta$ C-3a 36 1 ppm) and *trans*-1,3,3a,4,7,7a-hexahydro-2H-indene ($\delta$ C-3a 46.2 ppm), *cis* ($\delta$ C-3a 32 3 ppm) and *trans*-1,3,3a,4,7,7a-hexahydro-2H-inden-2-one ($\delta$ C-3a 38 9 ppm)[13] and **11** ($\delta$ C-3a 35.3, $\delta$ C-7a 33 8 ppm) is diagnostic for determining the regio- and the stereochemistry of the cyclization process

## EXPERIMENTAL SECTION

Melting points were obtained on a Reichert micro hotstage and are uncorrected. IR spectra were recorded as chloroform solutions $^1H$ and $^{13}C$ NMR spectra of $CDCl_3$ solutions were recorded at 200 1 and 50 3 MHz, respectively Column chromatography was executed on 0 063-0 200 mesh Merck silica gel All reactions were carried out under nitrogen, and all extracts were dried over $Na_2SO_4$

**Oxidation of diol 3b.** A solution of diol **3b**[4] (2 0 g, 4 7 mmol) in tetrahydrofuran (100 ml) was oxidized with periodic acid (2 28 g, 10 mmol) at room temperature for 4 h The reaction mixture was concentrated at reduced pressure (40 ml) and poured into water and extracted with chloroform The extract was washed with aqueous sodium hydrogen carbonate and water, dried and evaporated to dryness The residue was dissolved in acetone (100 ml) and treated with Jones' reagent[14] (10 mmol) at room temperature for 1 h The mixture was treated with excess 5% sodium bisulphite solution, diluted with water and extracted with chloroform The extract was dried and evaporated Chromatography of the residue and elution with chloroform-ethyl acetate (95 5) afforded semisolid acid **3c** (1 50 g, 79%), $^1H$ NMR $\delta$ 0 90, 1 03, 1 11 (each s, 9, methyls), 2 05 (s, 6, acetates), 4 19, 4 48 (4 lines AB, 2, J = 11Hz, $OCH_2$), 4 54 (m, 1, H-3), 5 35 (m, 1, H-7) Anal Calcd for $C_{23}H_{34}O_6$ C, 67 96, H, 8 43 Found C, 67 94, H, 8 46

**Oxidation of iso-virescenol diacetate 5a** To a mixture of N-methylmorpholine-N-oxide $2H_2O$ (1 6g, 14 mmol) in water (7 5 ml), acetone (7 5 ml) and osmium tetroxide (10 mg) in tert-butyl alcohol (3 ml), was added iso-virescenol B acetate **5a**[5] (3 30 g, 8 5 mmol) in tert-butyl alcohol (3 ml) The reaction was stirred at room temperature for 3 days A slurry of sodium hydrosulfite (100 mg), magnesium silicate (1 2 g), and water (8ml) was added, and the magnesol was filtered The filtrate was neutralizaed to pH 7 with a 1N solution of $H_2SO_4$, the acetone was evaporated under vacuum, the pH was further adjusted to pH 2 The solution was saturated with sodium chloride and extracted with chloroform The extract was dried and evaporated under reduced pressure The residue was dissolved in anhydrous tetrahydrofuran (100 ml) and treated with periodic acid (3 7g, 16 mmol) at room temperature for 6 h Workup as above, chromatography and elution with chloroform-ethyl acetate (95 5) yielded semisolid acid **5c** (2 0 g, 59%), $^1H$ NMR $\delta$ 0 95, 1 00, 1 21 (each s, 9, methyls), 2 00, 2 02 (each s, 6, acetates), 4 15, 4 32 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 54 (m, 1, H-3) Anal calcd for $C_{23}H_{34}O_6$ C, 67 96, H, 8 43 Found C, 67 89, H, 8 53

**Hydroboration-Oxidation of iso-virescenol B acetate 5a** A 1M boron hydride-tetrahydrofuran solution (5 ml) was added over 30 min-period to a stirring solution of iso-virescenol B acetate **5a** (3 60 g, 9 2 mmol), in anhydrous tetrahydrofuran (35 ml) at 0 °C The reaction mixture was allowed to warm at room temperature and stirred for additional 3 h It then was treated with water (3 ml), a 3N sodium hydroxide solution (4 ml) and a 36% hydrogen peroxide solution (3 6 ml), and the mixture was stirred at 60 °C for 1 h It was diluted with water, extracted with ethyl ether The extract was washed with water, dried, and evaporated Chromatography of the residue and elution with chloroform-ethyl acetate (95 5) gave starting material **5a** (100 mg) and the semisolid alcohol **5e** (2 20 g, 73%), $^1H$ NMR $\delta$ 0 92, 1 01, 1 08 (each s, 9, methyls), 2 03 (s, 6, acetates), 3 62 (m, 2, 2 H-16), 4 18, 4 48 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 55 (m, 1, H-3) Anal Calcd for $C_{24}H_{38}O_5$ C, 70 90, H, 9 42 Found C, 70 78, H, 9 53

**Acid 5f** The alcohol **5e** (1 10 g, 2 7 mmol) was dissolved in acetone (50 ml) and treated with Jones' reagent[14] (3 mmol) at room temperature for 1 h Workup as above, chromatography of the residue and elution with chloroform-ethyl acetate (19 1) afforded semisolid acid **5f** (0 90 g, 78%), $^1H$ NMR $\delta$ 1 00, 1 04, 1 05 (each s, 9, methyls), 2 06, 2 08 (each s, 6, acetates), 2 16, 2 27 (4 lines AB, 2, J = 17 Hz, 2 H-15), 4 19, 4 38 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 58 (m, 1, H-3) Anal Calcd for $C_{24}H_{36}O_6$ C, 68 55, H, 8 63 Found C, 68 71, H, 8 51

**Preparation of diazo ketones. General Procedure.** A solution of 10 mmol of unsaturated acid in 30 ml of methanol was neutralized by titration with a 0 1 N methanolic sodium methoxide solution to the phenolphthalein endpoint The mixture was evaporated under vacuum, and the residue was dried at 10 ml Torr and 100 °C for 1 h A suspension of the dry salt in 50 ml of anhydrous benzene was treated with 30 mmol of freshly distilled oxalyl chloride at O °C, and the mixture was stirred for 3 h It then was filtered, and the filtrate was evaporated under vacuum A solution of the residue in 100 ml of anhydrous ether was added dropwise over a 0 5-h period to a stirring solution of 13 mmol of diazomethane and 10 mmol of distilled triethylamine in 50 ml of dry ether at 0 °C, and the stirring was continued for 1-3 h The mixture was filtered, and the filtrate was evaporated Chromatography of the residue through a short column of neutral alumina (activity III) and elution with 25 1 hexane-ethyl acetate produced a diazo ketone, which was used in the next reaction without further purification

**Diazo ketone 3d.** Yellow, viscous liquid (57%), IR ($CHN_2$) 2100 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 0 90, 1 03, 1 10 (each s, 9, methyls), 2 06 (s, 6, acetates), 4 20, 4 50 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 55 (m, 1, H-3), 5 42 (m, 1, H-7), 5 52 (s, 1, $CHN_2$)

**Diazo ketone 5d.** Yellow, amorphous solid ( 58%), IR ($CHN_2$) 2104 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 0 98, 1 01, 1 15 (each s, 9, methyls), 2 02, 2 04 (each s, 6, acetates), 4 17, 4 32 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 55 (m, 1, H-3), 5 33 (s, 1, $CHN_2$)

**Diazo ketone 5g.** Yellow, viscous liquid (76 %), IR ($CHN_2$) 2100 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 1 00, 1 03, 1 04 (each s, 9, methyls), 2 05, 2 07 (each s, 6, acetates), 4 20, 4 38 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 58 (m, 1, H-3), 5 18 (s, 1, $CHN_2$)

**Diazo ketone 11** Yellow, viscous liquid (60%), IR ($CHN_2$) 2110, (C=O) 1630, $^1H$ NMR $\delta$ 1 20 - 2 23 (m, 6, methylens), 2 28 (d, 2, J = 7 Hz, -$CH_2$CO-), 5 24 (s, 1, $CHN_2$), 5 64 (bs, 2, olefinic protons)

**Diazo ketones decompositions. General Procedure.** A solution of 2 mmol of diazo ketone in 150 ml of methylene chloride was added dropwise over a 6-h period to a suspension of 0 04 mmol of dirhodium tetraacetate in 50 ml of methylene chloride The mixture was evaporated under vacuum Chromatography of the residue and elution with 30 1 hexane-ethyl acetate yield the cyclization products

**Keto ester 4.** Oil (53 %), IR (C=0) 1730 (s) cm $^{-1}$, $^1H$ NMR $\delta$ 0 88, 1 01, 1 12 (each s, 9, methyls), 2 05 (s, 6, acetates), 4 22, 4 48 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 55 (m, 1, H-3), 5 65 (m, 1, H-7), $^{13}C$ NMR $\delta$ 14 3 (10-Me) 19 5 (13-Me), 20 5 (C-11), 20 9, 21 0 ($OCO\underline{C}H_3$), 22 1 (4-Me), 23 7 (C-2), 23 9 (C-6), 30 1 (C-12), 35 3 (C-10), 37 1 (C-1), 39 0 (C-14), 40 6 (C-4), 48 0 (C-9), 49 5 (C-16), 50 2 (C-5), 62 3 (C-13), 64 1 ($OCH_2$), 79 9 (C-3), 123 3 (C-7), 134 3 (C-8), 170 3, 170 6 ($O\underline{C}OCH_3$), 213 0 (C-17) Anal Calcd for $C_{24}H_{34}O_5$ C, 71 61, H, 8 51 Found C, 71 58, H, 8 56

**Keto esters 6.** Oil (21 %), IR (C = O) 1740 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 1 03 (s, 3, 10-Me), 1 04 (s, 3, 4-Me), 1 11 (s, 3, 13-Me), 2 05, 2 08 (each s, 6, acetates), 2 23, 2 37 (4 lines AB, 2, J = 17 Hz, 2 H-14), 2 27 (d, 1, J = 17 Hz, H- -16), 2 77 (m, 1, H-11), 4 18, 4 34 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 57 (m, 1, H-3), $^{13}C$ NMR $\delta$ 19 4 (13-Me), 19 7 (C-6), 20 6 (10-Me), 21 1, 21 3 ($OCO\underline{C}H_3$), 22 7 (4-Me), 23 8 (C-2), 30 4 (C-11), 31 5 (C-7), 33 4 (C-1), 37 8 (C-10), 41 0 (C-4), 42 6 (C-14), 43 6 (C-16), 47 3 (C-13), 48 7 (C-16), 52 0 (C-5), 65 4 ($OCH_2$), 80 0 (C-3), 125 0 (C-8), 143 7 (C-9), 170 3, 170 8 ($O\underline{C}OCH_3$), 215 5 (C-17) Anal Calcd for $C_{24}H_{34}O_5$ C, 71 61, H, 8 51 Found C, 71 48, H, 8 64

**Keto ester 7.** Crystalline (52%), m p 134-136 °C, IR C=O 1725 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 0 94 (s, 3, 10-Me), 1 02 (s, 3, 4-Me), 1 13 (s, 3, 13-Me), 2 04, 2 07 (each s, 6, acetates), 4 22, 4 27 (4 lines AB, 2, $OCH_2$, 4 43 (m, 1, H-3), $^{13}C$ NMR $\delta$ 17 7 (C-6), 17 9 (10-Me), 17 9 (C-11), 19 1 (13-Me), 20 7, 20 8, ($OCO\underline{C}H_3$), 23 2 (4-Me), 23 5 (C-2), 27 2 (C-7), 34 2 (C-1), 35 4 (C-12), 35 9 (C-10), 36 2 (C-8), 38 6 (C-16), 40 7 (C-4), 41 5 (C-14), 42 7 (C-9), 46 0 (C-5), 51 4 (C-13), 64 5 ($OCH_2$), 79 4 (C-3), 169 9, 170 4 ($O\underline{C}OCH_3$), 215 2 (C-17) Anal Calcd for $C_{24}H_{34}O_5$ C, 71 61, H, 8 51 Found C, 71 45, H, 8 61

**Keto ester 8** Semisolid (40 %), IR (C=O) 1740 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 1 04, 1 05, 1 08 (each s, 9, methyls), 2 60 (dd, 1, J = 8,17 Hz, H-14) 4 20, 4 36 (4 lines AB, 2, J = 11 Hz, $OCH_2$), 4 58 (m, 1, H-3), $^{13}C$ NMR $\delta$ 19 5 (C-6), 19 6 (10-Me), 19 8 (C-11), 20 8, 20 9 ($OCO\underline{C}H_3$), 22 5 (4-Me), 24 0 (C-2), 26 1 (13-Me), 31 2 (C-12), 32 2 (C-7), 35 1 (C-1), 36 9 (C-10), 37 3 (C-13), 41 0 (C-4), 43 1 (C-15), 47 5 (C-14), 50 9 (C-17),

51 8 (C-5), 65 2 ($OCH_2$), 79 7 (C-3), 127 7 (C-8), 136 5 (C-9), 170 1, 170 6 ($O\underline{C}OCH_3$), 218 1 (C-16) Anal Calcd for $C_{25}H_{36}O_5$ C, 72 08, H, 8 71 Found C, 71 92, H, 8 81

**Keto ester 9.** Semisolid (27 %), IR (C=O) 1725 (s) $cm^{-1}$, $^1H$ NMR $\delta$ 0 96, (s, 3, 10-Me), 1 02 (s, 3, 4-Me), 1 08 (s, 3, 13-Me), 1 84 (bs, 2, 2 H-14) 2 03, 2 05 (each s, 6, acetates), 2 09, 2 21 (4 lines AB, 2, J = 14 Hz, H-15) , 2 41 (d, 2, J = 3 Hz, 2 H-17), 2 81 (m, 1, H-11), 4 14, 4 34 (4 lines AB, J = 11 Hz, $OCH_2$), 4 57 (m, 1, H-3); $^{13}C$ NMR $\delta$ 19 5 (10-Me), 19 5 (C-6), 20 9, 21 0 ($OCO\underline{C}H_3$),22 4 (4-Me), 23 8 (C-2), 31 4 (13-Me), 31 7 (C-7), 32 2 (c-11), 34 1 (C-1), 34 7 (C-13), 38 2 (C-10), 40 8 (C-4), 41 0 (C-12), 45 4 (C-15), 46 4 (C-14), 51 4 (C-5), 56 1 (C-17), 65 1 ($OCH_2$), 79 7 (C-3), 127 2 (C-8), 137 9 (C-9), 170 2, 170 7 ($O\underline{C}OCH_3$) 211 1 (C-16) Anal Calcd for $C_{25}H_{36}O_5$ C, 72 08, H, 8 71 Found C, 72 19, H, 8 63

**1,3,3a,6,7,7a,hexahydro-2H-inden-2-one 11**[12]. Colourless oil (53%), $^{13}C$ NMR $\delta$ 22 3 (C-7), 24 0 (C-6), 33 8 (C-7a), 35 3 (C-3a), 42 9 (C-3), 44 0 (C-1), 127 4 (C-5), 128 9 (C-4), 218 7 (C-2)

**Acknowledgment.** The Authors are indebted to the C N R (Rome) and the M U R S T for financial support and to F Castrica for technical assistance

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