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Isomerisation of 1-Methylene-2-methyl-2-(2-oxopropyl)-cyclohexanes to 2-Methylene-1-methyl-1-(2-oxopropyl)-cyclohexanes by Ene and Retro-ene Reaction

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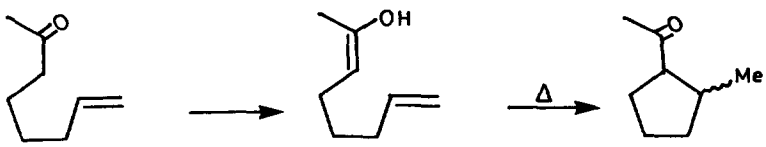
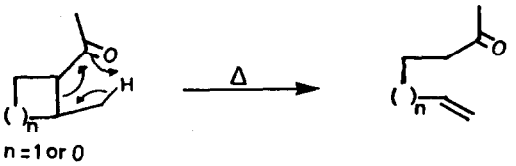
ABSTRACT: *Thermal activation of the normal Claisen products, the enones* **4**, **7** *and* **14** *in the presence of a catalytic amount of propionic acid generated the isomeric enones* **6**, **9** *and* **15** *via the sequential intramolecular ene-reaction of the enol tautomer followed by 1,5-hydrogen transfer (or retro ene-reaction) of the resultant acetyl cyclopropane intermediate. Conversion of the enones* **9** *and* **15** *into the corresponding cyclohexenones* **10** *and* **16** *established the structures of the rearrangement products.*

Organic compounds containing nonconjugated olefinic and carbonyl moieties are able to undergo considerable structural changes on thermal activation,[1] by intramolecular hydrogen displacement leading to ring closure. One such process is the intramolecular variant of general "ene" reaction.[2] The most significant example of the thermal behaviour of unsaturated carbonyl compounds is represented[3] by the thermal cyclisation of the oct-7-en-2-one system, in which four carbon atoms separate the olefin and carbonyl moieties, leading to a mixture of *cis* and *trans* 2-methylacetylcyclopentanes via ene reaction of the enol form, 2-hydroxyocta-2,7-diene (eq. 1). In the case of small ring systems like acylcyclopropanes and acylcyclobutanes, intramolecular hydrogen transfers are also thermally induced, leading to a retro ene reaction, and a ring opening occurs preferably (eq. 2).[4] A combination of these forward and reverse intramolecular ene reactions were postulated to explain the formation of the abnormal aromatic Claisen



(eq. 1)



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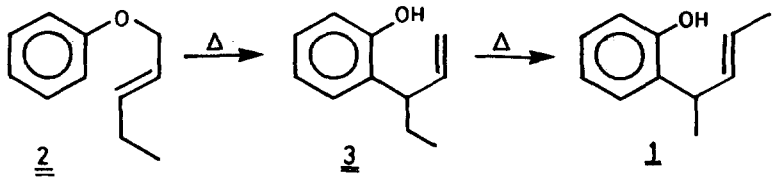
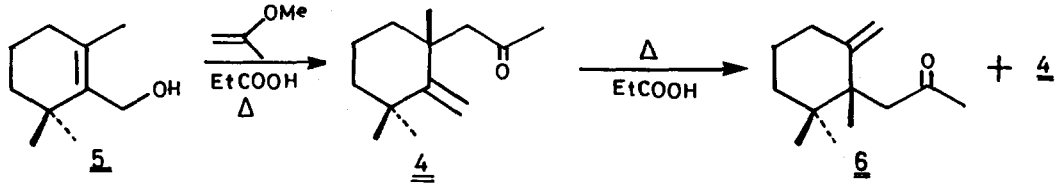


(eq. 3)

2 3 1

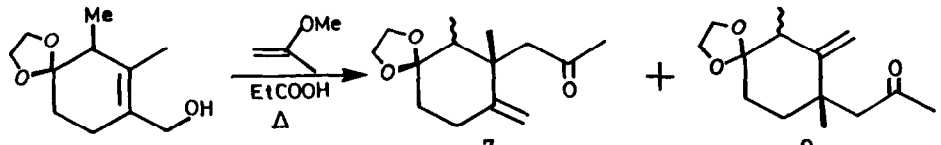
rearrangement products,[5] e.g. formation of the phenol 1 from the phenylether 2 via the normal Claisen product 3 (eq. 3).[5d] Based on these forward and reverse intramolecular ene-reactions,[6] herein we describe the propionic acid catalysed thermal isomerisation of 1-methylene-2-methyl-2-(2-oxopropyl)-cyclohexanes to 2-methylene-1-methyl-1-(2-oxopropyl)-cyclohexanes.



5 4 6

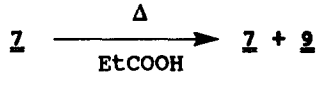
First thermolysis of the readily available[7] enone 4, the Claisen rearrangement product of cyclogeraniol (5) and 2-methoxypropene was investigated. Thermal activation (250°C) of the enone 4 in toluene in the presence of a catalytic amount of propionic acid furnished a ≈1:1 mixture of the starting enone 4 and the rearranged enone 6 in 75% yield, which was separated by silica gel column chromatography. The structure of the enone 6 was delineated from the spectral analysis in comparison with that of starting enone 4. The appearance of two broad singlets, due to the allylic coupling, for the two olefinic protons at δ 4.9 and 4.65, and in particular the upfield shift of the quaternary olefinic carbon resonance (δ 150 ppm) when compared to that of the starting enone (δ 160.5 ppm), due to the presence of only one fully substituted carbon on the olefin[8] instead of two as in 4, established the structure of the enone 6.

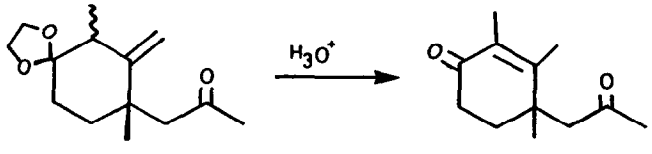
In order to establish, unambiguously the structure of the rearranged product, the enone 7, an intermediate used in the total synthesis[9] of homogynolide-B, was opted as starting material. Interestingly, the Claisen rearrangment of the allyl alcohol 8 was found to generate a mixture of the normal Claisen product 7 and the rearranged product 9. Thus, thermal activation of a solution of the allyl alcohol 8, 2-methoxypropene and a



8 7 9

catalytic amount of propionic acid in toluene in a Carius tube, first at 100°C for 12 hrs and later at 190°C for 48 hrs furnished a 3:2 epimeric mixture of the normal Claisen product **7** in 75% yield[9] and an epimeric mixture of the rearranged enone **9** in 11% yield. The minor product obtained in the Claisen rearrangement exhibited the ^{1}H NMR spectrum [δ 4.50-4.90 (2 H, m, C=CH_2), 3.66-4.16 (4 H, m, O–CH_2CH_2–O), 2.53 (2 H, s, CH_2–C=O), 2.10 and 2.00 (3 H, s, CH_3–C=O), 1.28 and 1.16 (3 H, s, *tert*-CH_3) and 1.06 ppm (3 H, d, J = 7.5 Hz, *sec*-CH_3)] similar to that of the enone **7**, for which the structure **9** was assigned based on the conversion of the enone **4** to **6**. Formation of the enone **9** from the enone **7** was readily established by thermal reaction of the enone **7**. Consequently thermal activation of a toluene solution of the enone **7** and a catalytic amount of propionic acid at 250°C for 48 hrs in a sealed tube furnished a 1:1 mixture of the enones **7** and **9** in 70% yield. Finally the structure of the enone **9** was unambiguously established from its conversion to the cyclohexenone **10**. Treatment of the enone **9** in CH_2Cl_2 with 2 N aqueous HCl furnished the α,β-unsaturated enone **10** in 90% yield *via* the hydrolysis of the ketal moiety and concomitant isomerisation of the olefin. The presence of absorption bands due to the saturated (1722) and α,β-unsaturated carbonyl groups (1662 cm^{-1}) in the IR spectrum, and the presence of a singlet at δ 2.16 due to an acetyl methyl, a singlet at 1.24 due to a *tert*-methyl and in particular two singlets at 1.80 and 1.86 ppm due to two olefinic methyl groups substituted at the α and β positions of the enone respectively in the ^{1}H NMR spectrum established the structure of the endione **10**, which was further confirmed by its ^{13}C NMR spectrum (see experimental section).

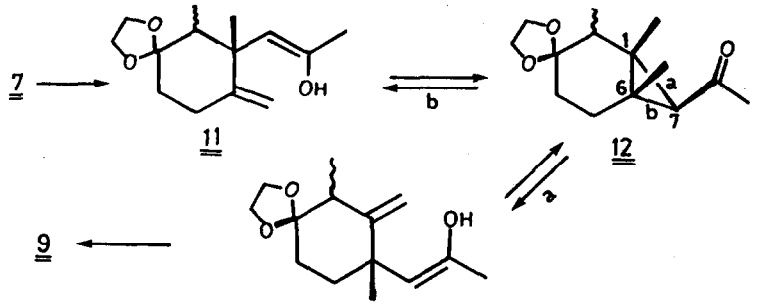




9 10

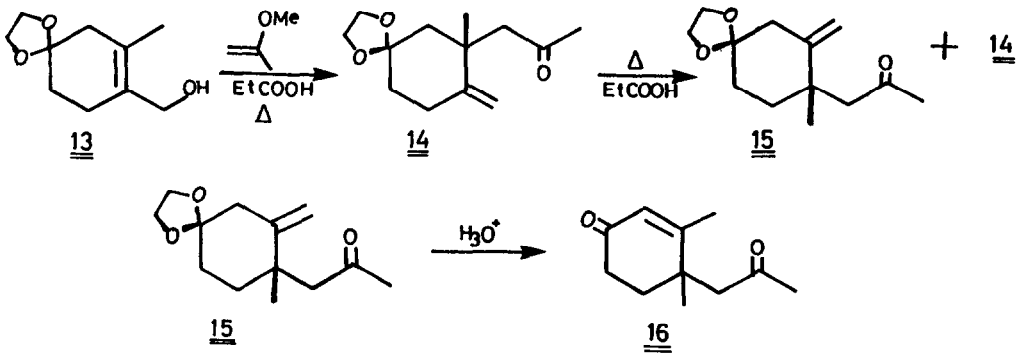
The formation of the enone **9** from the normal Claisen rearrangement product **7** can be readily explained as depicted in the scheme 1.

SCHEME 1



Intramolecular ene reaction of the enol tautomer **11** of the enone **7** forms the acetyl cyclopropane **12**. Thermal [1,5]-hydrogen transfer (or retro-ene reaction), either from the C_1-methyl or C_6-methyl to carbonyl oxygen *via* the cleavage of the corresponding cyclopropane bond (C_1–C_7 or C_6–C_7), furnishes either the rearranged enone **9** or the starting enone **7**.

In contrast to the allyl alcohol **8** but similar to cyclogeraniol (**5**),[7] the Claisen rearrangement of the allyl alcohol **13** under similar conditions, furnished only the normal Claisen product **14** with out the formation of any rearranged product. However, thermal activation of a toluene solution of the enone **14** and a catalytic amount of propionic acid at 250°C for 72 hrs furnished a 2:1 mixture of the starting and rearranged enones **14** and **15** in 80% yield establishing the generality. Acid catalysed hydrolysis of the rearranged enone **15** furnished the conjugated enone **16** confirming the structure of the enone **15**.



In conclusion, we have described here a novel rearrangement resulting in an interchange between exomethylene and quaternary carbon moieties on a cyclohexane ring, based on sequential forward and reverse intramolecular ene reactions of γ,δ-unsaturated enones via the corresponding enol forms. It is worth mentioning that the presence of a catalytic amount (≈3 μl) of

propionic acid is essential for this rearrangement to occur, as no product due to rearrangement was observed in the absence of propionic acid. On the other hand, increased amount of propionic acid (>10 μl) resulted in substantial amount of decomposition (low yields) along with the formation of side products *e.g.* intramolecular aldol type products, were observed. Finally, the hydrolytic conversion of the enones **9** and **15** into the cyclohexenones **10** and **16** respectively, unambiguously established the structures of the rearrangement products.

EXPERIMENTAL SECTION

IR spectra were recorded on Hitachi 270-50 and Perkin-Elmer 781 spectrophotometers. ^{1}H (90, 200 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded on Jeol FX-90Q and Brucker ACF-200 spectrometers. The chemical shifts (δ ppm) and the coupling constants (Hz) are reported in standard fashion with reference to either internal tetramethylsilane (for ^{1}H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra off-resonance multiplicities, when recorded, are given in parentheses. Low and High resolution mass measurements were carried out with a Jeol JMS-DX 303 GC-MS instrument using a direct inlet mode. Relative intensities of the ions are given in parentheses. All the starting allyl alcohols were prepared as per the procedures described earlier.[7,9] Acme's silica gel (100-200 mesh) and Qualigen's (Brockmann grade) neutral alumina were used for column chromatography.

1-(1,6,6-Trimethyl-2-methylenecyclohex-1-yl)-propan-2-one (6):

A solution of the enone **4** (194 mg, 1 mmol) and a catalytic amount of propionic acid in toluene (1 ml) was placed in a Carius tube, and heated to 250°C for 48 hrs. The reaction mixture was cooled, diluted with benzene (10 ml), washed with aqueous saturated $NaHCO_3$ (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of solvent and purification of the residue on a silica gel (10 g) column using ethyl acetate-hexane (1:40) as eluent first furnished the starting enone **4** (78 mg, 40%). Further elution of the column with the same solvent furnished the rearranged enone **6** (68 mg, 35%) as an oil. IR (neat): ν_{max} 1704, 1638, 1452, 1392, 1356, 1299, 1233, 1182, 1158, 897 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.9 (1 H, s) and 4.65 (1 H, s) ($C=CH_2$), 3.03 and 2.31 (2 H, AB q, J = 12.5 Hz, CH_2–C=O), 2.2 (2 H, m, allylic), 2.09 (3 H, s, CH_3–C=O), 1.0-1.8 (4 H, m), 1.11 (3 H, s), 0.89 (3 H, s) and 0.86 (3 H, s) (3 x CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 208.0 (s, C=O), 150.7 (s, $\underline{C}=CH_2$), 110.0 (t, $C=\underline{C}H_2$), 47.3 (t, $\underline{C}H_2$–C=O), 44.9 (s) and 37.4 (s) (C–1 and C–6), 36.5 (t, C–5), 32.9 (t, C–3), 31.5 (q, $\underline{C}H_3$–C=O), 24.4 (q), 23.1 (q) and 17.5 (q) (3 x CH_3), 22.9 (t, C–4). Mass: m/e 194 (M^+, 3%), 136 (60), 121 (36), 109 (70), 95 (70). HRMS: m/e Calcd. for $C_{13}H_{22}O$, 194.1671; Found, 194.1686.

cis & trans-2,3-Dimethyl-1,1-(ethylenedioxy)-4-methylene-3-(2-oxopropyl)-cyclohexanes (7) and cis & trans-2,4-dimethyl-1,1-(ethylenedioxy)-3-methylene-4-(2-oxopropyl)-cyclohexanes (9):

A solution of the allyl alcohol **8** (3.5 gms, 17.6 mmols), 2-methoxypropene (15 ml, 156 mmols), propionic acid (catalytic) in toluene (15 ml) were taken in four Carius tubes under nitrogen atmosphere and heated first at 100°C for 12 hrs, and latter at 190°C for 48 hrs. The Carius tubes were cooled, pooled, then diluted with ether (20 ml) and washed with saturated aqueous $NaHCO_3$ followed by brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a neutral alumina (20 gms) column using ethyl acetate-hexane (1:40) as eluent furnished a 3:2 diastereomeric mixture of the enone **7** (3.16 gms, 75%). IR (neat): ν_{max} 3070 (=C–H), 1700 (C=O), 1635 (C=C), 1440, 1350, 1170, 1140, 1080, 910 ($C=CH_2$) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 3:2 mixture of epimers): δ 4.88 (s) and 4.78 (s); and 4.88 (s) and 4.72 (s) (2 H, $C=CH_2$), 3.80-4.20 (4 H, m, $O-CH_2CH_2-O$), 1.40-3.30 (7 H, m), 2.10 and 2.12 (3 H, s, $CH_3-C=O$), 1.26 and 1.20 (3 H, s, *tert*-CH_3), 0.94 and 0.88 (3 H, d, J = 7.2 Hz, *sec*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, 3:2 mixture of epimers): δ 208.5 and 207.7 (s, C=O), 151.9 and 150.1 (s, $\underline{C}=CH_2$), 111.0 and 109.7 (s, O–C–O), 109.5 and 108.9 (t, $C=\underline{C}H_2$), 65.0 (t) and 63.7 (t); and 64.1 (t) and 63.3 (t) ($O-CH_2CH_2-O$), 51.7 (t), 49.4 and 41.9 (d, C–2), 46.4 (t), 42.4 (s, C–3), 36.0 and 32.0 (t, C–6), 31.5 and 29.8 (t, C–5), 30.4 (q, $\underline{C}H_3-C=O$), 23.3 and 23.0 (q, *tert*-CH_3), 11.4 and 7.7 (q, *sec*-CH_3). Mass: m/e 238 (30%, M^+), 209 (35), 181 (100, $M^+ - CH_2COCH_3$), 153 (47), 100 (25), 99 (53). HRMS: m/e For $C_{14}H_{22}O_3$ Calcd: 238.1569. Found: 238.1569.

Further elution of the column furnished the epimeric mixture of rearranged enone **9** (500 mg, 11%) as an oil. IR (neat): ν_{max} 3080 (=C–H), 1700 (C=O), 1630 (C=C), 1450, 3150, 1270, 1180, 1150, 1100, 1080, 1010, 950, 910 ($C=CH_2$) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, for major epimer): δ 4.83 (1 H, d, $J_{allylic}$ = 2 Hz) and 4.79 (1 H, d, $J_{allylic}$ = 2 Hz) (olefinic), 3.98 (4 H, m, $O-CH_2CH_2-O$), 1.86–2.90 (3 H, m), 2.19 (3 H, s, $CH_3-C=O$), 1.50-1.85 (4 H, m), 1.28 (3 H, s, *tert*-CH_3), 1.06 (3 H, d, J = 7.2 Hz, *sec*-CH_3). Mass: m/e 238 (25%, M^+), 223 (15, $M^+ - CH_3$), 181 (95, $M^+ - CH_2COCH_3$), 180 (40, $M^+ - CH_3COCH_3$), 136 (60), 129 (20), 121 (65), 101 (75), 100 (100), 99 (100).

Thermal activation of the enone 7:

A solution of the enone **7** (200 mg, 0.84 mmol) and a catalytic amount of propionic acid in toluene (1 ml) was placed in a Carius tube, and heated to 250°C for 48 hrs. The reaction mixture was cooled, diluted with benzene (10 ml), washed with aqueous saturated $NaHCO_3$ (10 ml) and dried over anhydrous Na_2SO_4. Evaporation of solvent and purification of the residue on a silica gel (10 g) column as described above furnished the starting enone **7** (70 mg, 37%) and the rearranged enone **9** (70 mg, 37%).

2,3,4-Trimethyl-4-(2-oxopropyl)-cyclohex-2-en-1-one (10):

To a solution of the enone **9** (240 mg, 1 mmol) in CH_2Cl_2 (5 ml), aqueous 2 N HCl (3 ml) was added and stirred vigorously at room temperature for 3 hrs. The organic layer was separated and the aqueous phase was extracted

with CH_2Cl_2 (5 ml). The combined organic phase was washed with saturated aqueous $NaHCO_3$ solution followed by brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel (2 gms) column using ethyl acetate-hexane (1:5) as eluent furnished the enone **10** (177 mg, 90%) as an oil. IR (neat): ν_{max} 1722 (saturated C=O), 1662 (enone C=O), 1452, 1380, 1257, 1209, 1101, 888, 795 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 2.76 and 2.54 (2 H, AB q, J = 14.4 Hz, $C\underline{H}_2$–$COCH_3$), 1.56-2.56 (4 H, m, H–5 and 6), 2.16 (3 H, s, CH_3–C=O), 1.86 (3 H, s, C_3–CH_3), 1.80 (3 H, s, C_2–CH_3), 1.24 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 206.9 (CH_3–$\underline{C}$=O), 198.0 (ring C=O), 159.6 (C–3), 131.1 (C–2), 51.3 ($\underline{C}H_2$–C=O), 38.6 (C–4), 34.0, 33.3, 32.0, 24.4, 16.5, 11.6. Mass: m/e 194 (5%, M^+), 176 (5), 137 (55, M^+ - CH_2COCH_3), 136 (100, M^+ - CH_3COCH_3), 121 (30), 109 (50), 93 (25). HRMS: m/e For $C_{12}H_{18}O_2$ Calcd : 194.1307. Found : 194.1303.

1,1-(Ethylenedioxy)-3-methyl-4-methylene-3-(2-oxopropyl)-cyclohexane (14):

The Claisen rearrangement of the allyl alcohol **13** (1 gm, 5.4 mmols), with 2-methoxypropene (5 ml, 52 mmols) and propionic acid (catalytic) in toluene (5 ml) at 180-190°C for 48 hrs as described for the allyl alcohol **8** followed by purification of the residue on a neutral alumina (20 gms) column using ethyl acetate-hexane (1:40) as eluent furnished the enone **14** (1.09 gms, 90%) as a colourless oil. IR (neat): ν_{max} 3060 (=C–H), 1700 (C=O), 1625 (C=C), 1435, 1345, 1110, 1080, 1035, 930, 910 (C=CH_2) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 4.83 (1 H, s) and 4.76 (1 H, s) (C=CH_2), 3.95 (4 H, s, O–CH_2CH_2–O), 2.75 (2 H, s, CH_2–C=O), 2.10 (3 H, s, CH_3–C=O), 1.30-2.60 (6 H, m), 1.24 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 207.4 (s, C=O), 152.0 (s, $\underline{C}$=CH_2), 108.1 (s, O–C–O), 107.8 (t, C=$\underline{C}H_2$), 64.0 (t) and 63.3 (t) (O–CH_2CH_2–O), 50.3 (t, $\underline{C}H_2$–C=O), 44.5 (t, C–2), 38.6 (s, C–3), 35.8 (t, C–6), 31.4 (q, $\underline{C}H_3$C=O), 29.9 (t, C–5), 25.3 (q, *tert*-CH_3). Mass: m/e 224 (M^+, 15%), 181 (15, M^+ - CH_3CO), 167 (100, M^+ – CH_2COCH_3), 139 (30), 99 (40).

Thermal activation of the enone 14:

Thermal reaction of the enone **14** (300 mg, 1.3 mmol) and a catalytic amount of propionic acid in toluene (1 ml) at 250°C for 72 hrs as described for the enone **7** followed by purification of the residue on a silica gel (10 g) column using ethyl acetate-hexane (1:40) as eluent first furnished the starting enone **14** (160 mg, 53%). Further elution of the column with the same solvent furnished the rearranged enone **15** (80 mg, 27%) contaminated with small amount of intramolecular aldol type product, as an oil. IR (neat): ν_{max} 3070, 1705, 1635, 1350, 1170, 1080, 945, 890 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 4.85 (1 H, s) and 4.82 (1 H, s) (C=CH_2), 4.02 (4 H, s, –OCH_2CH_2O–), 2.5 (2 H, s, CH_2–C=O), 2.17 (3 H, s, CH_3–C=O), 1.4-2.0 (6 H, m), 1.29 (3 H, s, *tert*-CH_3). Mass: m/e 206 (M^+, 10%), 167 (70, M^+ - CH_2COCH_3), 120 (60), 105 (35), 99 (100).

3,4-Dimethyl-4-(2-oxopropyl)-cyclohex-2-en-1-one (16):

Hydrolysis of the enone **15** (40 mg, 0.19 mmol) in CH_2Cl_2 (2 ml) with aqueous 2 N HCl (2 ml) at room temperature for 3 hrs as described for the enone **9** followed by purification of the product on a silica gel (2 gms) column using ethyl acetate-hexane (1:5) as eluent furnished the pure enone

16 (21 mg, 60%) as an oil. IR (neat): ν_{max} 1710 (saturated C=O), 1660 (enone C=O), 1355, 1230, 1160 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 5.85 (1 H, br s, olefinic), 2.80 and 2.58 (2 H, AB q, J = 18 Hz, $C\underline{H}_2$–$COCH_3$), 1.55-2.55 (4 H, m, H–5 and 6), 1.93 (3 H, d, J = 1.5 Hz, olefinic CH_3), 1.30 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 206.6 (s, CH_3–$\underline{C}$=O), 198.8 (s, ring C=O), 167.6 (s, C–3), 126.7 (d, C–2), 50.9 (t, $\underline{C}H_2$–C=O), 37.7 (s, C–4), 33.9 (t, C–6), 33.5 (t, C–5), 31.6 (q, $\underline{C}H_3$–C=O), 24.2 (q, olefinic CH_3), 20.2 (q, *tert*–CH_3).

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