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$Rh_2(OAc)_4$-Mediated Decomposition Of Diazocarbonyl Compounds: A Comparison Of α-Diazo Ketones And α-Diazo β-Keto Esters Reactivity.

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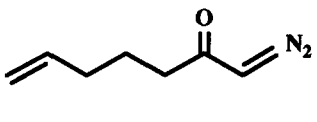
Abstract: Unsaturated α-diazocarbonyl compounds undergo intramolecular cyclopropanation or carbon-hydrogen bond insertion when catalyzed by $Rh_2(OAc)_4$: α-diazo ketones react preferentially with carbon-carbon double bond, whereas closely related α-diazo-β-keto-esters insert into carbon-hydrogen bond.

Introduction

Carbenoids generated by interaction of dirhodium tetraacetate and α-diazocarbonyl compounds are capable of inserting in an intramolecular sense into carbon-hydrogen bond or carbon-carbon double bond, in carbon-carbon bond forming reactions. The intramolecular carbon-hydrogen insertion reaction favours the formation of 5-membered carbocycles and the process proved to be high yielding and selective.[1] Methines are more reactive for insertion than methylenes, which in turn are more reactive then methyles.[2] A benzylic site is less reactive than an aliphatic one carrying the same substitution,[2a] electron-withdrawing groups can deactivate a carbon-hydrogen insertion.[3] Unsaturated carbenoids exhibit different reactivity as regards the position of carbon-carbon double bond. Rhodium mediated decomposition of α,β-unsaturated α-diazo ketones generates cyclopentenones through intramolecular γ-carbon-hydrogen insertion.[4] Diazo ketones prepared from α-alkyl α,β-unsaturated acids, thus exposing two γ-carbon sites to the carbenoid center, exhibit a strong preference in the formation of cyclopentenones respect to α-alkylidencyclopentanones.[5] β,γ-unsaturated α-diazo ketones undergo skeletal rearrangement to γ,δ-unsaturated acids.[6] Competition between carbon-hydrogen insertion and cyclopropanation was observed in rhodium mediated decomposition of γ,δ-unsaturated diazocarbonyl compounds.[2a,7] Finally α-diazo esters bearing a remote carbon-carbon double bond give only carbon-hydrogen insertion products.[2a]

In the course of a general program in natural cyclopentanoids synthesis it becomes interesting to use 3-vinyl-cyclopentanone **2** from which to elaborate the requisite functionality. Following previous reports (e.g. **3** → **4**),[2a] and as a result of our interest in the utilization of the α-diazocarbonyl function for intramolecular anullation reactions, we decided to prepare **2** by decomposition of readly available diazo ketone **1**. Much to our surprise, treatment of **1** with dirhodium tetraacetate provided not a trace of ketone **2** as evidenced by the lack of vinyl protons in the ^1H NMR spectrum of the crude product. There was obtained a 83% of a liquid compound, which was assigned structure **5**[8] on the basis of NMR data.



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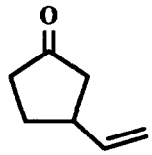

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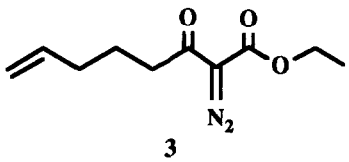

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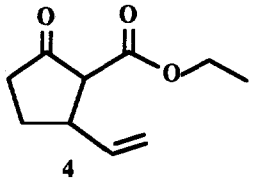

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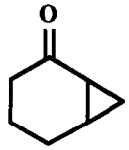

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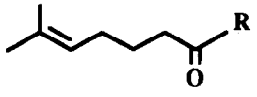
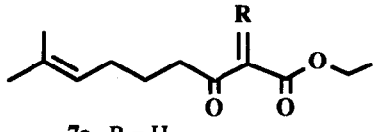
Discussion

The behaviour of **1** and **3** accounts as well for a different electrophilic character of carbenoids generated by interaction of α-diazo ketones and α-diazo β-keto esters with dirhodium tetraacetate. In an effort to delineate the reactivity of these functional groups respect to the same catalyst we have undertaken a more through investigation.

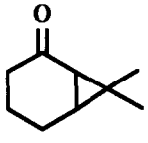
In this initial study we chose as models a pair of unsaturated diazo compounds with a more substituted double bond, the 7-methyl-1-diazo-6-octen-2-one **6b** and the methyl 2-diazo-6-methyl-3-oxo-hepta-5-enoate **7b**. Compounds **6b** and **7b** were prepared from the acid **6a**[9] and the ketoester **7a**.[10] Interaction of **6b** and **7b** with dirhodium tetraacetate afforded the cyclopropyl derivative **8** (67%) and cyclopentanone **9** (60%) respectively. Once again the carbenoid generated from an α-diazo ketone preferred to interact with the carbon-carbon double bond forming a cyclopropane ring.



6a R = OH
6b R = CHN_2



7a R = H_2
7b R = N_2



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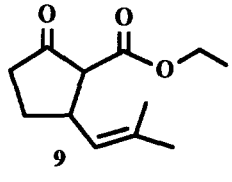

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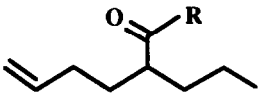
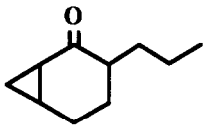
Likewise α-alkyl unsaturated diazo ketones generated mainly cyclopropanation products. Thus **10b**, prepared from the acid **10a**,[11] afforded a mixture of compounds from which the cyclopropane dervative **11** were separated in 54% yield (*exo* and *endo* isomers). Besides these products the cyclopentanones **12** (16%)

and **13** (14%), each as pair of steroisomers, were obtained. Taber reported[2a] that the decomposition of the closely related α-diazo β-keto ester **14** yielded only carbon-hydrogen bond insertion products (**15** and **16**). The ^{13}C NMR spectra of **11** supported the presence of a cyclopropane system by the observation of three tertiary aliphatic carbon signals. Heteronuclear carbon-hydrogen correlation allowed carbons and protons assignments to be made. The configuration at C-3 of **11** was determined by comparison with carbon shift values of **5**, acting as model. The observed multiplicity of the methyl group in ^1H NMR spectrum of **12** and **13** is diagnostic for structure determination. The stereochemistry of these compounds was established by comparison with ^{13}C chemical shift values of 2,4-disubstituted cyclopentanones.[12]



10a R = OH
10b R = CHN_2



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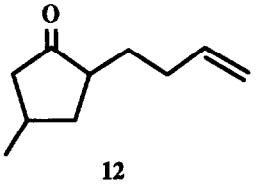

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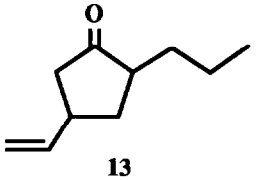

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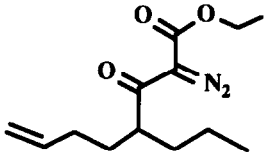

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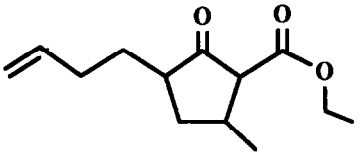

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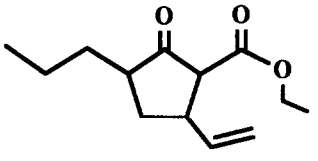

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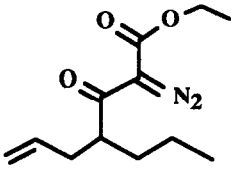
The same reactivity trend was also observed for γ,δ-unsaturated diazo ketones and diazo β-keto esters. Thus, while diazo ester **17** afforded cyclopropyl derivative **18** and cyclopentanone **19** in 1:0.4 ratio,[2a] diazo ketone **20b** [13] was transformed into a mixture of cyclization products in which the cyclopropane derivative **21** (*exo* and *endo* isomers) was largely represented (56%). Careful column chromatography allowed to separate beside **21** a little amount of cyclopentanone **22** (5%).



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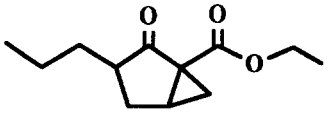

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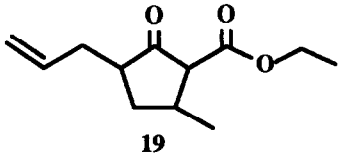

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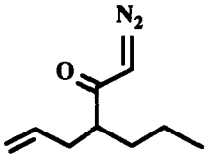
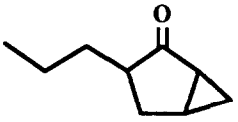


20 a R = OH
20 b R = CHN_2



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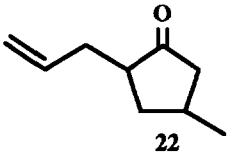

22

All the systems that have been examined possess a freely rotating aliphatic side chain therefore the observed reactivity cannot be governed by steric and conformational effects. Carbenoids generated by interaction of copper catalysts and α-diazo ketones or α-diazo β-keto esters, exhibit a strong preference toward a soft nucleophile, such as carbon-carbon double bond.[14] Decomposition of α-diazo ketones with dirhodium tetraacetate generates carbenoids soft enough to interact faster with a carbon-carbon double bond. The presence of an ester function at the carbenoid centre increases the electrophilic character so much that the interaction with a hard nucleophile such as a carbon-hydrogen bond becomes generally the preferred pathway.

The most interesting aspect of the present results is that selective rhodium carbenoid insertion reaction can be predicted choosing α-diazo ketones or α-diazo β-keto esters bearing a remote double bond as precursors.

EXPERIMENTAL SECTION

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 chromatrography was executed on 70-230 mesh Merck silica gel. All reactions were carried out under nitrogen, and all extracts were dried over Na_2SO_4.

Ethyl 8-methyl-3-keto-7-nonenoate (7a). Preparation was effected by the method of Weiler.[10] To a solution of diisopropylamine (1.3 ml, 9 mmol) in tetrahydrofuran (6 ml), cooled at -78 °C a hexane solution (2.5 M) of n-butyllithium (3.5 ml, 8.4 mmol) was added. The temperature was brought to -10 °C for 15 min, and then recooled to -78 °C. A solution of methyl acetoacetate (0.38 ml, 3.5 mmol) in tetrahydrofuran (2 ml) was added dropwise via siringe over 10 min. The cooling bath was removed, the mixture was stirred for 45 min and then 1-bromo-4-methyl-3-pentene (2 g, 12.2 mmol) was added. Stirring was continued for 30 min, and then the reaction was quenched with 10% aqueous hydrochloric acid and extracted with ether.
The combined organic extracts were concentrated in vacuo. The residual oil chromatographed on silica gel with 49:1 hexane-ethyl acetate gave 0.45 g (61 %) of liquid ester **7a**. ^1H NMR δ 1.28 (t, 3, J = 7 Hz, $COOCH_2$-$C\underline{H}_3$), 1.58 and 1.68 (s, 6, methyls), 2.00 (m, 2, $C\underline{H}_2$-CH=C), 2.53 (t, 2, J = 7 Hz, $C\underline{H}_2COCH_2COOEt$), 3.44 (s, 2, $COC\underline{H}_2COOEt$), 4.2 (q, 2, J = 7 Hz $COOC\underline{H}_2CH_3$), 5.08 (m, 1, olefinc proton). Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.02; H, 9.36.

2-*n*-Propyl-5-hexenoic acid (10a). To a suspension of sodium hydride (0.5 g, 10.2 mmol) in benzene-dimethylformamide (1:1) (6 ml) dimethyl malonate was added (1.16 ml, 10.2 mmol) in benzene (6

ml) at room temperature and the mixture stirred for 1 h. Then 1-bromo-3-butene (3.37 g, 25 mmol) was added and the mixture stirred for 24 h. The mixture was poured into water and extracted with ether. The combined organic layers were dried and evaporated under vacuum. The residue dissolved in benzene (8 ml) was added to a suspension of sodium hydride (0.5 g, 10.2 mmol) in benzene-dimethylformamide (1:1) (6 ml) and the mixture stirred for 1 h. After this period 1-bromo-propane (3.07 g, 25 mmol) was added and the mixture stirred for 24 h. Workup as above gave the crude diester which was treated with a mixture of sodium chloride (1.24 g, 24.6 mmol), water (0.7 ml) and dimethyl sulphoxide (21 ml) at reflux for 4 h. Water was added and the mixture was extracted with ether. The combined organic layers were washed with water, dried and evaporated under vacuum. A solution of the crude ester in a 12 % ethanolic solution of potassium hydroxide (150 ml) was kept at 40 °C for 8 h and then reduced to a 60 ml volume by vacuum distillation. It was poured into 140 ml of water and extracted with chloroform. The aqueous solution was acidified with a 2 % sulfuric acid solution and extracted with chloroform. The extracts were washed with water, dried and evaporated. Chromatography of the residue and elution with 25:1 chloroform - etyl acetate yielded 0.92 g (58 %) of amorphous solid acid **10a**. ^{1}H NMR δ 0.92 (t, 3, J = 7 Hz, methyl), 4.91 - 5.12 (m, 2, olefinic methylene), 5.70 - 5.91 (m, 1, olefinic methine). Anal. Calcd. for $C_6H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.92; H, 10.46.

Preparation of Diazoketones. Freshly distilled oxalyl chloride (2.50 g, 20 mmol) was added dropwise to a stirring solution of 10 mmol of unsaturated acid in dry methylene chloride (15 ml) at 35 °C and the stirring continued for 2 h. The solution was evaporated under vacuum and the residual unsaturated acid chloride dissolved in dry ether (100 ml). The solution 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 anhydrous ether (50 ml) at 0 °C and the stirring continued for 2 h. The mixture was filtered and the filtrate evaported. Chromatography of the residue through a short column of neutral alumina (activity III) and elution with 25:1 hexane-ethyl acetate led to diazoketone, which was used in the next reaction without further purification.

1-Diazo-6-hepten-2-one (1): (61 %), pale yellow, viscous liquid; IR CHN_2 2850 (m), $C{=}N_2$ 2080 (s), C=O 1615 (s) cm^{-1}. ^{1}H NMR δ 1.06 - 2.05 (m, 6, methylenes), 4.08 - 5.15 (m, 2, olefinic methylene), 5.20 (s, 1, CHN_2), 5.50 - 5.90 (m, 1, olefinic methine).

7-Methyl-1-diazo-6-octen-2-one (6b): (58 %), pale yellow, viscous liquid; IR CHN_2 2860 (m), $C{=}N_2$ 2100 (s), C=O 1625 (s) cm^{-1}. ^{1}H NMR δ 1.60, 1.68 (s, 3 each, methyls), 1.80 - 2.43 (m, 6, methylenes), 5.10 (t, 1, J = 6 Hz, olefinic proton), 5.25 (s, 1, CHN_2).

3-*n*-Propyl-1-diazo-6-hepten-2-one (10b): (65 %), yellow, viscous liquid; IR CHN_2 2860 (m), $C{=}N_2$ 2110 (s), C=O 1625 (s) cm^{-1}; ^{1}H NMR δ 0.90 (t, 3, J = 7 Hz, methyl), 1.09 - 2.42 (m, 9, methylenes and methyne), 5.00 (m, 2, olefinic methylene), 5.21 (s, 1, $\underline{CH}N_2$), 5.68 (m, 1, olefinic methine).

3-*n*-Propyl-1-diazo-5-hexen-2-one (20b): (51 %), yellow, amorphous solid; IR CHN_2 2862 (m), $C{=}N_2$ 2100 (s), C=O 1620 (s) cm^{-1}; ^{1}H NMR δ 0.83 (t, 3, J = 7 Hz, methyl), 1.05 - 2.50 (m, 7, methylenes and methine), 5.05 (m, 2, olefinic methylene), 5.21 (s, 1, CHN_2), 5.62 (m, 1, olefinic methine).

Ethyl 8-Methyl-2-diazo-3-keto-7-nonenoate (7b): A mixture of ester **7a** (0.5 g, 2.3 mmol) and tosyl azide[11] (0.64 g, 2.3 mmol) was stirred in THF (5 ml) with 1 g of KF on alumina[15] at 0 °C for 16 h. After filtration, the solid was washed with THF and ether was added to the filtrate. The organic layer was washed with a 2 % aqueous solution of KOH, dried and evaporated. The residue was filtered on neutral alumina giving 0.55 g (98 %) of liquid ester **7b**, IR C=N_2 2160 (s), CO_2Et 1720 (s), C=O 1650 (s) cm^{-1}; ^{1}H NMR δ 1.30 (t, 3, J = 7 Hz, $CH_2\underline{CH_3}$), 1.68, 1.70 (s, 3 each, methyls), 1.50 - 2.30 (m, 4, methylenes), 2.85 (t, 2, J = 6 Hz, CO$\underline{CH_2}$), 4.32 (q, 2, J = 7 Hz, $\underline{CH_2}CH_3$), 5.21 (t, 1, J = 6 Hz, olefinic proton).

Decomposition of Diazo compounds. A solution of 2 mmol of diazo derivative in methylene chloride (150 ml) 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 yielded the reaction product.

Bicyclo[4.1.0]heptan-2-one (5)[8]: (83 %); ^{1}H NMR δ 1.02 - 2.38 (m, 10, methylenes and methines), ^{13}C NMR 9.7 (C-7), 17.0 (C-6), 17.5 (C-4), 20.9 (C-5), 25.3 (C-1), 39.3 (C-3), 208.2 (C-2).

7-Dimethyl-bicyclo[4.1.0]heptan-2-one (8): (67 %), colorless oil; ^{1}H NMR δ 1.14 (s, 3, Me), 1.15 (s, 3, Me), 1.36 - 2.25 (m, 8, methylenes and methines), ^{13}C NMR δ 16.7 (*endo* Me), 18.8 (C-4), 25.7 (C-5), 27.5 (C-7), 29.3 (*exo* Me), 30.8 (C-6), 34.5 (C-1), 39.9 (C-3), 209.6 (C-2). Anal. Calcd. for $C_9H_{14}O$: C, 88.45; H, 11.55. Found: C, 88.51; H, 11.49.

Ethyl 5-(*i*-But-1-enyl)-cyclopentan-2-one-carboxylate (9): (60 %), colorless oil; ^{1}H NMR δ 1.18 (t, 3, $CH_2\underline{CH_3}$), 1.62 (d, 3, J = 1 Hz, Me), 1.64 (d, 3. J = 1 Hz, Me), 1.4 - 2.4 (m, 4, methylenes), 2.80 (d, 1, J = 13 Hz, H-2), 3.32 (m, 1, H-3), 4.10 (q, 2, $\underline{CH_2}$-CH_3), 4.98 (m, 1, olefinic proton), ^{13}C NMR δ 14.0 (-CH_2-$\underline{CH_3}$), 17.9 (C-8), 25.4 (C-9), 28.0 (C-4) 37.9 (C-5), 40.4 (C-3), 60.9 (O-CH_2), 61.8 (C-2), 125.4 (C-6), 134.4 (C-7), 168.8 (C-10), 211.0 (C-1). Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.48; H, 8.66.

3-*n*-Propyl-bicyclo[4.1.0]heptan-2one (11) and 2-(1-But-3-enyl)-4-methyl-cyclopentanone (12) and 2-*n*-Propyl-4-ethenyl-cyclopentanone (13): **(11)** colorless oil; ^{1}H NMR δ 0.68 (t, 3, J = 7 Hz, Me), 0.85 - 2.1 (m, 13, methylenes and methines), *exo* (40%) ^{13}C NMR δ 13.7 (C-10), 13.9 (C-7), 18.1 (C-6), 19.9 (C-9) 20.1 (C-5), 24.7 (C-1), 26.6 (C-4), 31.9 (C-8), 43.7 (C-3), 210.9 (C-2); *endo* (14%) ^{13}C NMR δ 7.8 (C-7), 13.7 (C-10), 16.4 (C-6), 19.5 (C-9), 21.0 (C-5), 21.6 (C-4), 25.4 (C-1), 32.9 (C-8), 46.3 (C-3), 210.6 (C-2); Anal. Calcd. for $C_{10}H_{14}O$: C, 89.49; H, 10.51. Found: C, 89.52; H, 10,44. **(12)**[16] *cis* (10 %) colorless oil;^{1}H NMR δ 0.87 (t, 3, J = 7 Hz, Me), 1.2 - 3 (m, 10, methylenes and methines), 4.9 - 5.6 (m, 3, olefinic protons), ^{13}C NMR δ 13.9 (C-8), 20.6 (C-7), 31.6 (C-6), 36.2 (C-3), 38.7 (C-4), 44.2 (C-5), 49.8 (C-2), 114.1 (C-10), 140.6 (C-9), 220.9 (C-1); *trans* (6 %), colorless oil; ^{1}H NMR δ 0.87 (t, 3, J = 7 Hz, Me), 1.0 - 3.0 (m, 10, methylenes and methines), 4.8 - 5.6 (m, 3, olefinic proton), ^{13}C NMR δ 13.9 (C-8), 20.6 (C-7), 31.6 (C-6), 37.9 (C-3), 38.6 (C-4), 43.6 (C-5), 46.5 (C-2), 113.9 (C-10), 140.2 (C-9), 219.5 (C-1). Anal. Calcd. for $C_{10}H_{14}O$: C, 89.49; H, 10.51. Found: C, 89.54; H, 10.46. **(13)**[16] *cis* (9 %), colorless oil; ^{1}H NMR δ 1.12 (d, 3,

J = 7 Hz, Me), 1.2 - 2.6 (m, 10, methylenes and methines), 4.9 - 5.9 (m, 3, olefinic protons), ^{13}C NMR δ 20.2 (C-10), 28.8 (C-7), 29.5 (C-4), 31.5 (C-6), 38.4 (C-3), 46.7 (C-5), 50.1 (C-2), 114.9 (C-9), 138.0 (C-8), 220.0 (C-1); *trans* (5 %), colorless oil; ^1H NMR δ 1.08 (d, 3, J = 7 Hz, Me), 1.2 - 2.6 (m, 10, methylenes and methines), 4.8 - 5.8 (m, 3, olefinic protons), ^{13}C NMR δ 20.7 (C-10), 28.1 (C-4), 28.8 (C-7), 31.5 (C-6), 36.7 (C-3), 46.4 (C-5), 46.1 (C-2), 115.0 (C-9), 137.9 (C-8), 218.9 (C-1). Anal. Calcd. for $C_{10}H_{14}O$: C, 89.49; H, 10.51. Found: C, 89.61; H, 10.44.

3-*n*-Propyl-bicyclo[3.1.0]hexan-2-one (21) and 2-(1-Prop-2-enyl)-4-methyl-cyclopentanone (22): (21)[16] *exo* (56 %), colorless oil; ^1H NMR δ 0.72 (m, 1, H-6 *endo*), 0.82 (t, 3, J = 7, Me), 1.10 (m, 1, H-7), 1.15 (m, 1, H-6 *exo*), 1.25 (m, 2, H-8), 1.53 (m, 1, H-7), 1.65 (m, 1, H-3 *endo*), 1.75 (m, 1, H-5), 1.91 (m, 1, H-4), 2.15 (m, 1, H-2), 2.35 (m, 1, H-3 *exo*), ^{13}C NMR δ 13.6 (C-9), 13.7 (C-6), 19.8 (C-5), 21.5 (C-8), 28.3 (C-1), 29.0 (C-4), 36.2 (C-7), 46.0 (C-3), 217.1 (C-2); *endo* (20 %), colorless oil; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, Me), 0.95 (m, 1, H-6 *endo*), 1.15 (m, 1, H-7), 1.17 (m, 1, H-6 *exo*), 1.23 (m, 2, H-8), 1.68 (m, 1, H-7), 1.71 (m, 1, H-3 *endo*), 1.78 (m, 1, H-5), 1.97 (m, 1, H-4), 1.98 (m, 1, H-2), 2.26 (m, 1, H-3 *exo*); ^{13}C NMR δ 13.9 (C-9), 14.4 (C-6), 19.8 (C-5), 20.4 (C-8), 27.5 (C-1), 30.2 (C-4), 31.7 (C-7), 40.1 (C-3), 216.0 (C-2). Anal. Calcd. for $C_9H_{14}O$: C, 88.45; H, 11.55. Found: C, 88.61; H, 11.42. **(22)** (5 %), colorless oil; ^1H NMR δ 1.14 (d, 3, Me), 1.2 - 2.65 (m, 8, methylenes and methines), 5.55 (m, 2, olefinic methylene), 5.75 (m, 1, olefinic methine), ^{13}C NMR δ 20.3 (C-6), 28.3 (C-4), 33.9 (C-7), 37.9 (C-3), 46.8 (C-5), 50.4 (C-2), 116.3 (C-9), 135.9 (C-8), 221.0 (C-1). Anal. Calcd. for $C_9H_{14}O$: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.41.

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