102. Fragmentation of Homoallylic Alkoxides. Preparation of 1-(3′-Cyclopentenyl)-2-alkanones from 2-Substituted Bicyclo[2.2.1]hept-5-en-2-ols[1])

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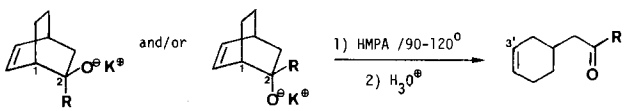
Summary

The potassium 2-substituted bicyclo[2.2.1]hept-5-en-2-alkoxides derived from alcohols **2–9** at 30° in hexamethylphosphoric triamide (HMPA) afford 1-(3′-cyclopentenyl)-2-alkanones **10–19** *via* heterolytic C(1),C(2)-allylic bond cleavage in the substrate alkoxide followed by intramolecular protonation of the resultant transient allylic anion.

Introduction. – Recently we described the thermolysis of a series of potassium 2-substituted bicyclo[2.2.2]oct-5-en-2-alkoxides which resulted in the selective formation of 1-(3′-cyclohexenyl)-2-alkanones in moderate to high yields [1] *(Scheme 1)*. This reaction is believed to proceed *via* an initial, heterolytic C(1),C(2)-bond cleavage followed by a regioselective, intramolecular protonation of the resultant, transient allylic anion. As part of a programme to investigate the preparative value of this novel transformation[2]) for other bicyclic systems it was decided to study the behaviour of an analogous series of potassium 2-substituted bicyclo-[2.2.1]hept-5-en-2-alkoxides.

Scheme 1



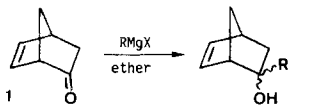
Results and discussion. – Treatment of bicyclo[2.2.1]hept-5-en-2-one (**1**) with the appropriate *Grignard* reagent afforded a series of epimeric 2-substituted bicyclo-[2.2.1]hept-5-en-2-ols, **2–9**, in which the *endo*-epimer is, in all cases, the major

[1]) Presented, in part, at the Meeting of the Swiss Chemical Society in Bern, October 16, 1981.

[2]) This reaction is an example of a homoallylic alkoxide fragmentation. For another synthetic application, the preparation of propenyl ketones from carboxylic esters, see [2].

component ($\geqslant 90\%$[3])) *(Scheme 2)*. In our hands these epimeric alcohol pairs were not cleanly separable by column chromatography and the mixtures were added to a slurry of a 10% excess of potassium hydride in hexamethylphosphoric triamide (HMPA) at 0–5° under N_2 to form their corresponding potassium alkoxides.

Scheme 2



endo / exo (≥10:1)

	R	Yield %
2	CH_3	88
3	C_2H_5	62
4	C_3H_7	27[4]
5	i-C_3H_7	12[4]
6	$CH_2CH{=}CH_2$	92
7	$CH_2C(CH_3){=}CH_2$	91
8	$CH_2C_6H_5$	88
9	C_6H_5	76

Without isolation these were then heated at 30° prior to a standard aqueous workup. For the majority of substrates the formation of a 1-(3′-cyclopentenyl)-2-alkanone, *via* C(1), C(2)-allylic bond cleavage, is the principal reaction pathway *(cf. Table)*.

The potassium alkoxides derived from the 2-methyl, 2-ethyl, 2-propyl and 2-isopropyl bicyclic alcohols **2–5** afforded the 3-cyclopentenyl ketones **10–13**, together with small amounts ($\leqslant 10\%$) of their 2-cyclopentenyl isomers (*cf.* experiments 1–4). In addition to the fact that the reaction conditions are mild (30°/48 h[5])), almost certainly a result of the C(1), C(2)-bond strain in the substrate alkoxides, it is noteworthy that substantial epimerisation of the substrate is observed during the reaction[6]). These results are consistent with a non-concerted reaction pathway in which reversible heterolytic cleavage of the C(1), C(2)-allylic bond forms a transient allylic anion which is then irreversible quenched, in the rate-determining step, by intramolecular capture of a proton adjacent to the carbonyl group. The resulting potassium enolate subsequently affords the 3-cyclopentenyl ketone by external protonation[7]) (*cf. Scheme 3*, pathway **a**). The high selectivity (*ca.* 90%) with respect to the position of the cyclopentenyl double bond may be rationalised by the strong

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[3]) GC. analysis was used to determine isomer ratios; the high stereoselectivity favouring the *endo*-epimer demonstrates the preferential attack of the *Grignard* reagent on the sterically less encumbered *exo*-face of **1**, see [3].

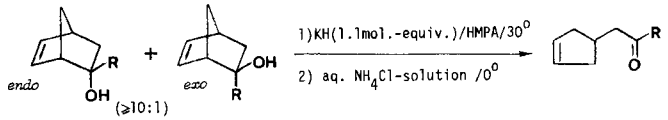
[4]) These low yields are due to competing reduction of **1** to *endo*- and *exo*-bicyclo[2.2.1]hept-5-en-2-ols by hydride transfer [4].

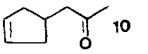
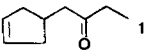
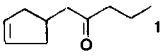
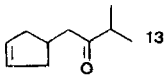
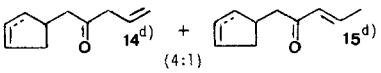
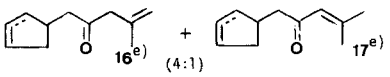
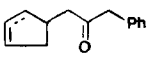
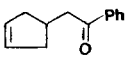
[5]) Attempted use of a higher reaction temperature (50°) to avoid the long reaction times gave lower yields and substantial polymerisation.

[6]) This was observed by quenching aliquots during the reaction. For example, at the end of the reaction the unreacted alcohol mixture (*ca.* 10%) consisted of a 4:1 *exo/endo* isomer ratio (*cf. Exper. Part*). This behaviour is in contrast to the fragmentation reactions of analogous bicyclo-[2.2.2]oct-5-en-2-alkoxides where only partial epimerisation was observed *cf.* [1].

[7]) In analogy with previous work [1] the potassium enolate degenerates to its parent ketone under the reaction conditions, presumably by protonation by the solvent.

Table. *Formation of the cyclopentenyl-alkanones* **10–19**



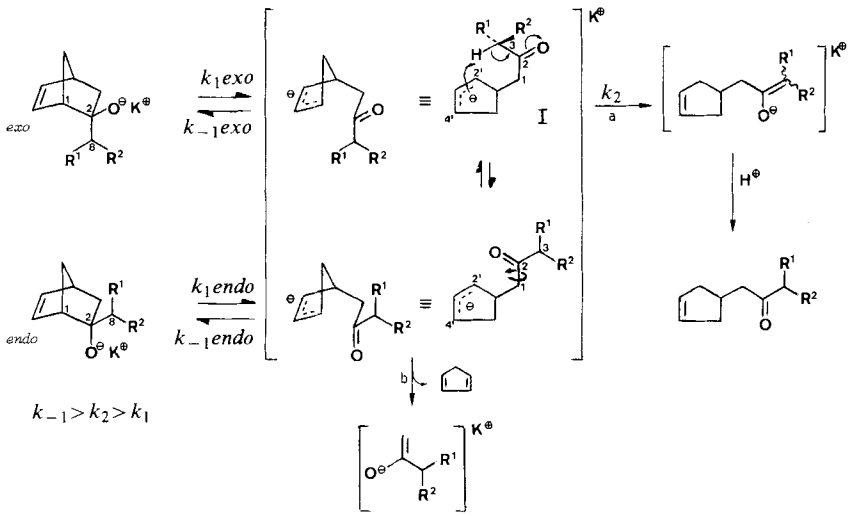
Exp.	Substrate[a])	R	Reaction Time	Products[b])	Yield[c]) %
1	**2**	CH_3	48 h	 **10**	45
2	**3**	C_2H_5	48 h	 **11**	50
3	**4**	C_3H_7	48 h	 **12**	48
4	**5**	i-C_3H_7	48 h	 **13**	21
5	**6**	$CH_2CH=CH_2$	24 h	 **14**[d]) + **15**[d]) (4:1)	71
6	**7**	$CH_2C(CH_3)=CH_2$	24 h	 **16**[e]) + **17**[e]) (4:1)	76
7	**8**	$CH_2C_6H_5$	24 h	 **18**[f])	85[g])
8	**9**	C_6H_5	1 h	 **19**	8[h])

[a]) 10 mmol substrate. [b]) Structures confirmed by spectral data (IR., ^{1}H- and ^{13}C-NMR. and MS.); ≤ 10% 2-cyclopentenyl isomer. [c]) Conversion ≥ 90%; yields, not optimised, refer to distilled products. [d]) Contains *ca.* 40% 2-cyclopentenyl isomer. [e]) Contains *ca.* 15% 2-cyclopentenyl isomer. [f]) Contains *ca.* 30% 2-cyclopentenyl isomer. [g]) 1-Phenyl-2-propane (6%) also isolated. [h]) Acetophenone (62%) also isolated.

preference for intramolecular proton transfer from the C(3)-position to the C(2′)-position of the allylic anion *via* the six-membered transition state provided by conformation **I**[8]). Despite the fact that 1-(3′-cyclopentenyl)-2-alkanones are the only

[8]) The C(2′)-position is also preferred to the C(4′)-position for proton capture from the C(1)-position *cf.* **9** → **19** *(vide infra).*

Scheme 3



isolable reaction products their only moderate yields merit comment. The probable explanation is a competing *retro-Diels-Alder* reaction in which successive cleavages of the C(1),C(2)- and C(3),C(4)-bonds in the substrate afford cyclopentadiene and a potassium enolate which may then further interact to form polymeric products (*cf. Scheme 3*, pathway **b**)[9]). Support for this hypothesis is provided by the isolation of 1-phenyl-2-propanone in experiment 7 and acetophenone in experiment 8 *(vide infra).*

In the same manner but under slightly milder conditions (30°/24 h) the potassium alkoxides prepared from the 2-allyl, 2-(2-methallyl) and 2-benzyl substituted alcohols **6**–**8** furnished the 3-cyclopentenyl ketones **14** and **15** (*ca.* 15% 2-cyclopentenyl isomer), **16** and **17** (*ca.* 40% 2-cyclopentenyl isomer) ((4:1)-mixtures of the β,γ- and α,β-unsaturated ketones) and **18** (30% 2-cyclopentenyl isomer)[10]) in high yield (*cf.* experiments 5, 6 and 7). Several observations are worthy of mention. Firstly, and in contrast to experiments 1–4, the selectivity with regard to the cyclopentenyl double bond position is decreased. The reason for this is not completely clear. One plausible explanation is that, owing to the increased acidity of the C(3)-protons, enolatisation may now be partially effected intermolecularly by the alkoxide substrate. The regenerated substrate alcohol would then quench non-selectively the allylic anion. This hypothesis is consistent with the ready reversibility of the C(1),C(2)-bond cleavage which ensures an appreciable concentration of alkoxide during the reaction. Secondly, these reactions are site-selective, *i.e.* C(1),C(2)-bond cleavage occurs to the exclusion of the alternative C(2),C(8)-bond

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[9]) For an example of a concerted *retro-Diels-Alder* reaction involving the magnesiumbromo alkoxide of *endo*-bicyclo[2.2.1]hept-5-en-2-ol see [5].

[10]) A small amount (6%) of 1-phenyl-2-propanone was also isolated. This ketone results from the competing *retro-Diels-Alder* reaction.

cleavage, an expected result of the relatively higher energy of the former bond[11]). Finally, the increased reaction rate and product yield are the logical consequences of a more rapid intramolecular enolatisation due to the higher acidity of the C(3)-protons in the intermediate allylic anion.

Treatment of the potassium alkoxides prepared from the 2-phenyl-substituted alcohol **9**, in HMPA, at 30° during 1 h led to the isolation of acetophenone (62%) together with the 3-cyclopentenyl ketone **19** (8%) (*ca.* 10% 2-cyclopentenyl isomer). The predominance of the *retro-Diels-Alder* reaction product, acetophenone, is doubtless due to both the increased rate of this reaction and the decreased rate of intramolecular protonation in the absence of C(3)-protons. The fact that the selectivity with regard to the cyclopentenyl double bond is retained indicates that intramolecular proton transfer from the C(1)- to the C(2′)-position is preferred to the alternative C(1)- to C(4′)-proton transfer.

In conclusion, it has been demonstrated that 1-(3′-cyclopentenyl)-2-alkanones may be prepared selectively, in moderate yields, from readily available 2-substituted bicyclo[2.2.1]hept-5-en-2-ols under relatively mild reaction conditions[12])[13]). Given the increasing need for specifically functionalised cyclopentenes in synthesis it is hoped that this new synthetic method will be applicable to more complex systems. Further investigations in this direction are under study.

Experimental Part

(with the collaboration of *M. Wüst*)

1. General. – All solvents were dried and distilled before use. Each reaction was followed by TLC. and GC. analysis. Workup refers to: successive washing of the combined org. phase with H_2O, sat. aq. $NaHCO_3$- and sat. aq. NaCl-solution, drying of the org. phase (anh. Na_2SO_4) and removal of the solvent *i.v.* Thin layer chromatography (TLC.) with CH_2Cl_2 as eluent was performed using *Merck* 0.25 mm *(60 F 254)* silica gel plates. Preparative chromatography (column) was carried out on silica gel (*Merck*, 0.06–0.20 mm). Gas chromatograms (GC.): 4 atm. N_2; glass columns (3 mm ID, 3 m), stationary phase on *Chromosorb W* (acid washed, 80/100 mesh): 5% *Carbowax*. Capillary columns: 0.7 atm. He; *UCON* (52 m). Melting points (m.p.) are uncorrected. Boiling points (b.p.) using a bulb-to-bulb apparatus, refer to the oven temperature (bath) and pressure (Torr). IR. (*Perkin-Elmer A 21* spectrometer) spectra: liquid film unless otherwise specified, ν max. in cm^{-1}. NMR. spectra: in $CDCl_3$, internal standard tetramethylsilane ($\delta = 0$ ppm); abbreviations: s = singlet, d = doublet, t = triplet, qa = quadruplet, m = multiplet, br. = broad, J = spin-spin coupling constant (Hz). ^{1}H-NMR. at 60 MHz *(Varian A 60)* or 360 MHz *(Bruker WH 360)*. ^{13}C-NMR. at 90.5 MHz. Mass spectra (MS.) *Atlas CH 4;* electron energy: 70 eV, signals are given in m/z (rel. %).

2. Preparation of bicyclo[2.2.1]hept-5-en-2-one (*1*). – A solution of cyclopentadiene (66 g, 1.0 mol) and 2-chloroacrylonitrile (100 g, 1.14 mol) in 150 ml of toluene containing hydroquinone (0.5 g) was heated under N_2 at 80° during 24 h in an autoclave. Concentration of the mixture gave a residual oil (158 g) which was dissolved in 500 ml of EtOH and added dropwise to a stirred solution of KOH (168 g, 3 mol) in 2 l of EtOH. The mixture was refluxed for 1 h, cooled and 500 ml of H_2O was added.

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[11]) The absence of **1**, the product of C(2),C(8)-allylic bond cleavage, was rigorously proven.

[12]) A direct approach *via* a thermal, intramolecular *retro*-ene reaction of the *endo*-bicyclo[2.2.1]hept-5-en-2-ol (5% benzene solution, 300°/4 h) led to extensive polymerisation and only trace amounts (< 10%) of the 1-(3′-cyclopentenyl)-2-alkanone.

[13]) A similar synthetic transformation is the *retro-Norrish* Type II photochemical reaction of *endo*-bicyclo[2.2.1]hept-5-en-2-ol to give (3-cyclopentenyl)acetaldehyde, see [6].

Neutralisation with 120 ml of glacial acetic acid was followed by removal of the EtOH by distillation at 730 Torr. Extraction (ether) of the residue, workup and fractional distillation afforded **1** as a colourless oil (24.8 g, 23%), m.p. 21–23° (lit.[7]: 22–23°). – B.p. 52–55°/12 Torr. – IR.: 1740, 1420, 1325, 990, 940, 860, 770. – ^{1}H-NMR.: 1.80–2.40 (4 H); 3.03 and 3.20 (*m*, 2 H); 6.16 and 6.60 (*m*, 2 H). – MS.: 108 (17, $C_7H_8O^+$), 91 (1.4), 79 (8), 66 (100), 51 (1.4), 39 (8).

3. Preparation of alcohols *2–9*. – *General procedure.* Alcohols **2–5** and **9** were prepared on a 25 mmol scale by the addition of an ethereal solution of **1** to a 10% excess of the methyl, ethyl, propyl, isopropyl and phenyl *Grignard* reagents (freshly-prepared from the appropriate alkyl/aryl halide and Mg) in ether, followed by reflux during 1 h. Alcohols **6–8** were prepared using *Barbier* conditions (also on a 25 mmol scale), *i.e.* a solution of 2-allyl, 2-methallyl or benzyl chloride (10% excess) and **1** was added to a stirred slurry of Mg in refluxing ether. After 1 h the mixture was poured into cold sat. aq. NH_4Cl-solution. Extraction (ether), workup and column chromatography (cyclohexane/ethyl acetate) was followed by distillation *i.v.* Estimation of *endo-/exo*-isomer ratios was effected by GC. analysis.

3.1. *2-Methylbicyclo[2.2.1]hept-5-en-2-ol* (**2**) (*endo/exo* = 15:1) [8]. Yield 88%, b.p. 130° (bath)/ 0.5 Torr. – TLC.: Rf 0.22. – IR.: 3400 br., 3060, 2870, 1280, 1260, 1070, 838, 770. – ^{1}H-NMR.: 1.00–2.00 (4 H); 1.23 (*s*, 3 H); 1.67 (*s*, 1 H, D_2O addition removes this signal); 2.67 (*m*, 1 H); 2.84 (*m*, 1 H); 6.32 (*m*, 2 H). – MS.: 124 (7, $C_8H_{12}O^+$), 109 (1), 81 (5), 66 (100), 58 (8), 43 (18).

3.2. *2-Ethylbicyclo[2.2.1]hept-5-en-2-ol* (**3**) (*endo/exo* = 15:1). Yield 62%, b.p. 130° (bath)/0.5 Torr. – TLC.: Rf 0.24. – IR.: 3450 br., 3060, 2880, 1460, 1340, 1280, 1000, 960, 730, 715. – ^{1}H-NMR.: 0.85–2.05 (9 H); 1.47 (*s*, 1 H, D_2O addition removes this signal); 2.80 (*m*, 2 H); 6.32 (*m*, 2 H). – MS.: 138 (3, $C_9H_{14}O^+$), 109 (19), 81 (6), 72 (12), 66 (100), 57 (9), 43 (8).

3.3.*2-Propylbicyclo[2.2.1]hept-5-en-2-ol* (**4**) (*endo/exo* = 15:1). Yield 27%, b.p. 130° (bath)/0.4 Torr. – TLC.: Rf 0.28. – IR.: 3450 br., 3070, 2880, 1340, 1280, 1010, 970, 830. – ^{1}H-NMR.: 0.80–2.10 (11 H); 1.43 (*s*, 1 H, D_2O addition removes this signal); 2.80 (*m*, 2 H); 6.32 (*m*, 2 H). – MS.: 152 (4, $C_{10}H_{16}O^+$), 109 (20), 86 (7), 71 (12), 66 (100), 58 (41), 43 (16).

3.4. *2-Isopropylbicyclo[2.2.1]hept-5-en-2-ol* (**5**) (*endo/exo* = 15:1). Yield 12%, b.p. 130° (bath)/ 0.4 Torr. – TLC.: Rf 0.34. – IR.: 3500 br., 3070, 2880, 1358, 1275, 1190, 964, 780, 730, 710. – ^{1}H-NMR.: 0.85–2.10 (11 H); 1.33 (*s*, 1 H, D_2O addition removes this signal); 2.87 (*m*, 2 H); 6.31 (*m*, 2 H). – MS.: 152 (1.5, $C_{10}H_{16}O^+$), 109 (42), 86 (18), 81 (11), 71 (39), 66 (100), 43 (21).

3.5. *2-Allylbicyclo[2.2.1]hept-5-en-2-ol* (**6**) (*endo/exo* = 15:1). Yield 92%, b.p. 140° (bath)/0.4 Torr. – TLC.: Rf 0.30. – IR.: 3450 br., 3070, 1640, 1340, 1280, 1175, 915, 838, 722. – ^{1}H-NMR.: 0.90–2.35 (4 H); 1.70 (*s*, 1 H, D_2O addition removes this signal); 2.50 (*d*, J = 7, 2 H); 2.77 (*m*, 2 H); 5.01 and 5.22 (*m*, 2 H); 6.00 (*m*, 1 H); 6.30 (*m*, 2 H). – MS.: 150 (1, $C_{10}H_{14}O^+$), 109 (33), 81 (12), 79 (9), 66 (100), 56 (5), 41 (13).

3.6. *2-(2-Methylallyl)bicyclo[2.2.1]hept-5-en-2-ol* (7) (*endo/exo* = 15:1). Yield 91%, b.p. 140° (bath)/0.4 Torr. – TLC.: Rf 0.40. – IR.: 3500 br., 3070, 1640, 1340, 1280, 1120, 1060, 834, 770, 725. – ^{1}H-NMR.: 0.90–2.10 (4 H); 1.60 (*s*, 1 H, D_2O addition removes this signal); 2.50 (br. *s*, 2 H); 2.80 (*m*, 2 H); 4.87 (*m*, 2 H); 6.30 (*m*, 2 H). – MS.: 164 (0.5, $C_{11}H_{16}O^+$), 109 (14), 108 (15), 98 (1.5), 83 (12), 66 (100), 56 (13).

3.7. *2-Benzylbicyclo[2.2.1]hept-5-en-2-ol* (**8**) (*endo/exo* = 15:1). Yield 88%, b.p. 180° (bath)/ 0.2 Torr. – TLC.: Rf 0.41. – IR.: 3570 br., 3470 br., 1500, 1450, 1340, 1280, 1120, 1080, 830, 730, 700. – ^{1}H-NMR.: 0.85–2.15 (4 H); 1.50 (*s*, 1 H, D_2O addition removes this signal); 2.80 (*m*, 2 H); 3.07 (br. *s*, 2 H); 6.27 (*m*, 2 H); 7.30 (*m*, 5 H). – MS.: 200 (23, $C_{14}H_{16}O^+$), 134 (39), 116 (22), 109 (67), 91 (57), 81 (24), 66 (100), 43 (29).

3.8. *2-Phenylbicyclo[2.2.1]hept-5-en-2-ol* (**9**) (*endo* [9]/*exo* [8] = 10:1). Yield 81%, b.p. 150° (bath)/ 0.1 Torr. – TLC.: Rf 0.34. – IR.: 3450 br., 2880, 1500, 1445, 1340, 1270, 1175, 1130, 990, 730, 700, 660. – ^{1}H-NMR.: 1.33 and 1.56 (*m*, 2 H); 1.87 (*s*, 1 H, D_2O addition removes this signal); 2.47 (*m*, 2 H); 2.93 (*m*, 1 H); 3.20 (*m*, 1 H); 6.41 (*m*, 2 H); 7.42 (*m*, 5 H). – ^{13}C-NMR. (*endo*-**9**): 147.4 (*s*); 140.8 (*d*); 133.7 (*d*); 128.0 (*d*); 126.9 (*d*); 126.3 (*d*); 82.0 (*s*); 53.3 (*d*); 49.1 (*t*); 44.7 (*t*); 43.3 (*d*). – MS.: 186 (3, $C_{13}H_{14}O^+$), 120 (98), 105 (33), 91 (3), 77 (23), 66 (100), 51 (7).

4. Preparation of ketones *10–19* (*cf. Table*). – The preparation and fragmentation of the potassium alkoxides of the alcohols **2–9** (*endo/exo* $\geq$ 10:1) (*cf.* experiments 1–8) were performed using the following standard procedure. A solution of the alcohol (10 mmol) in HMPA (5 ml) was added dropwise, during 20 min., to a stirred slurry of potassium hydride (*Alfa:* 24.1% in mineral oil; 1.1 mol.-equiv.) in HMPA (20 ml) at 0–5° under N_2. After 30 min the mixture was allowed to stir at 30° during the specified time, cooled and then poured into an excess of cold sat. aq. NH_4Cl-solution. Isolation of the reaction products

was effected by extraction (ether), workup (removal of ether at 760 Torr), column chromatography (CH_2Cl_2) and distillation *i.v.*

4.1. *1-(3'-Cyclopentenyl)-2-propanone* (**10**)[14]. Yield 45%, b.p. 100° (bath)/0.5 Torr. – TLC.: Rf 0.50. – IR.: 3050, 2850, 1715, 1620, 1410, 1360, 1180, 1156, 940, 700. – ^{1}H-NMR.: 1.70–2.80 (7 H); 2.12 (*s*, 3 H); 5.66 (*s*, 2 H). – ^{13}C-NMR.: 208.4 (*s*); 129.6 (*d*); 50.5 (*t*); 38.9 (*t*); 32.7 (*d*); 30.1 (*qa*). – MS.: 124 (16, $C_8H_{12}O^+$), 109 (1.2), 79 (3), 66 (100), 58 (7), 43 (39). Also isolated was recovered **2** (*endo/exo* = 1:4, 8%).

4.2. *1-(3'-Cyclopentenyl)-2-butanone* (**11**)[14]. Yield 50%, b.p. 100° (bath)/0.5 Torr. – TLC.: Rf 0.60. – IR.: 3060, 2850, 1715, 1620, 1420, 1370, 1120, 950, 700. – ^{1}H-NMR.: 1.05 (*t*, *J* = 7, 3 H); 1.93 (*m*, 2 H); 2.42 (*qa*, *J* = 7, 2 H); 2.51 (*d*, *J* = 7, 3 H); 2.57 (*m*, 2 H); 2.69 (*m*, 1 H); 5.66 (*s*, 2 H). – ^{13}C-NMR.: 211.1 (*s*); 129.6 (*d*); 49.1 (*t*); 38.9 (*t*); 36.1 (*t*); 32.7 (*d*); 7.8 (*qa*). – MS.: 138 (11, $C_9H_{14}O^+$), 109 (24), 81 (13), 67 (25), 66 (100), 57 (30). Also isolated was recovered **3** (*endo/exo* = 1:4, 7%).

4.3. *1-(3'-Cyclopentenyl)-2-pentanone* (**12**)[14]. Yield 48%, b.p. 120° (bath)/0.5 Torr. – TLC.: Rf 0.63. – IR.: 3060, 2850, 1710, 1620, 1410, 1370, 1125, 1030, 740. – ^{1}H-NMR.: 1.91 (*t*, *J* = 7, 3 H); 1.60 (*t* × *qa*, *J* = 7, 2 H); 1.92 (*m*, 2 H); 2.36 (*t*, *J* = 7, 2 H); 2.50 (*d*, *J* = 7, 2 H); 2.56 (*m*, 2 H); 2.69 (*m*, 1 H); 5.66 (*s*, 2 H). – MS.: 152 (0, $C_{10}H_{16}O^+$), 109 (0.4), 86 (51), 84 (68), 74 (17), 59 (30), 49 (100). Also isolated was recovered **4** (*endo/exo* = 1:4, 7%).

4.4. *1-(3'-Cyclopentenyl)-3-methyl-2-butanone* (**13**)[14]. Yield 21%, b.p. 120° (bath)/0.5 Torr. – TLC.: Rf 0.65. – IR. (in $CDCl_3$): 3060, 2850, 1705, 1620, 1465, 1364, 1030, 680. – ^{1}H-NMR.: 1.09 (*d*, *J* = 7, 6 H); 1.90 (*m*, 2 H); 2.60 (*d*, *J* = 7, 2 H); 2.54 (*m*, 1 H); 2.58 (*m*, 2 H); 2.69 (*m*, 1 H); 5.66 (*s*, 2 H). – MS.: 152 (7, $C_{10}H_{16}O^+$), 109 (62), 86 (26), 81 (43), 71 (49), 66 (100).

4.5. *1-(3'-Cyclopentenyl)-4-penten-2-one* (**14**)[15]) and *(E)-1-(3'-cyclopentenyl)-3-penten-2-one* (**15**)[15]) (4:1-mixture). Yield 71%.

Data of **14**. B.p. 130° (bath)/0.5 Torr. – TLC.: Rf 0.61. – IR.: 3060, 2850, 1715, 1640, 1402, 1366, 1000, 920. – ^{1}H-NMR.: 1.93 (*m*, 2 H); 2.56 (*d*, *J* = 7, 2 H); 2.57 (*m*, 2 H); 2.69 (*m*, 1 H); 3.17 (*d*, *J* = 7, 2 H); 5.12–5.21 (2 H); 5.66 (*s*, 2 H); 5.93 (*m*, 1 H). – MS.: 150 (1.5, $C_{10}H_{14}O^+$), 109 (67), 81 (52), 67 (100), 53 (8), 41 (44).

Data of **15**. B.p. 130° (bath)/0.5 Torr. – TLC.: Rf 0.48. – IR. (in $CDCl_3$): 3050, 2850, 1670, 1630, 1440, 1290, 975, 670. – ^{1}H-NMR.: 1.90 (*m*, 3 H); 1.95 (*m*, 2 H); 2.56 (*m*, 2 H); 2.62 (*d*, *J* = 7, 2 H); 2.70 (*m*, 1 H); 5.66 (*s*, 2 H); 6.13 (*d*, *J* = 15, 1 H); 6.84 (*d* × *qa*, *J* = 15 and 7, 1 H). – MS.: 150 (6, $C_{10}H_{14}O^+$), 135 (4), 122 (3), 109 (10), 84 (76), 69 (100).

4.6. *1-(3' and 2'-Cyclopentenyl)-4-methyl-4-penten-2-one* (**16**)[16]) *and 1-(3'- and 2'-cyclopentenyl)-4-methyl-3-penten-2-one* (**17**)[16]) (4:1 mixture). Yield 76%.

Data of **16**. B.p. 130° (bath)/0.5 Torr. – TLC.: Rf 0.63. – IR.: 3060, 2850, 1710, 1650, 1440, 1404, 1200, 900. – ^{1}H-NMR.: 1.75 (*s*, 3 H); 1.93 (*m*, 2 H); 2.57 (*m*, 2 H); 2.57 (*d*, *J* = 7, 2 H); 2.69 (*m*, 1 H); 3.10 (*s*, 2 H); 4.82 and 4.95 (2 H); 5.66 (*s*, 2 H). – MS.: 164 (5, $C_{11}H_{16}O^+$), 109 (49), 98 (7), 81 (100), 67 (68), 55 (22).

Data of **17**. B.p. 130' (bath)/0.5 Torr. – TLC.: Rf 0.54. – IR.: 3060, 2850, 1685, 1620, 1440, 1380, 1110, 1036, 685. – ^{1}H-NMR.: 1.90 (*s*, 3 H); 1.96 (*m*, 2 H); 2.16 (*s*, 3 H); 2.51 (*d*, *J* = 7, 2 H); 2.57 (*m*, 2 H); 2.69 (*m*, 1 H); 5.66 (*s*, 2 H); 6.08 (*m*, 1 H). – MS.: 164 (3, $C_{11}H_{16}O^+$), 134 (1), 109 (5), 98 (39), 83 (100), 67 (12), 55 (23).

4.7. *1-(3'- and 2'-Cyclopentenyl)-3-phenyl-2-propanone* (**18**)[17]). Yield 85%, b.p. 180° (bath)/0.4 Torr. – TLC.: Rf 0.67. – IR.: 3060, 3040, 2850, 1710, 1602, 1500, 1456, 1364, 1044, 700. – ^{1}H-NMR.: 1.86 (*m*, 2 H); 2.54 (*m*, 2 H); 2.56 (*d*, *J* = 7, 2 H); 2.67 (*m*, 1 H); 3.68 (*s*, 2 H); 5.62 (*s*, 2 H); 7.19–7.36 (5 H). – MS.: 200 (18, $C_{14}H_{16}O^+$), 134 (22), 109 (100), 91 (50), 81 (74), 67 (93).

Also isolated was 1-phenyl-2-propanone. Yield 6%, b.p. 120° (bath)/0.1 Torr. – TLC.: Rf 0.53. – IR. (in $CDCl_3$): 3040, 1710, 1500, 1360, 1230, 700. – ^{1}H-NMR.: 2.15 (*s*, 3 H); 3.69 (*s*, 2 H); 7.28 (*m*, 5 H). – MS.: 134 (19, $C_9H_{10}O^+$), 91 (51), 65 (9), 43 (100).

4.8. *2-(3'-Cyclopentenyl)acetophenone* (**19**)[14]). Yield 8%, b.p. 160° (bath)/0.3 Torr (lit.[10]: 60–62°/0.1 Torr). – TLC.: Rf 0.70. – IR.: 3050, 2850, 1675, 1600, 1440, 1210, 990, 750. – ^{1}H-NMR.: 2.04 (*m*, 2 H); 2.64 (*m*, 2 H); 2.87 (*m*, 1 H); 3.08 (*d*, *J* = 7, 2 H); 5.70 (*s*, 2 H); 7.44–7.58 and 7.97 (5 H). – MS.: 186 (7, $C_{13}H_{14}O^+$), 120 (100), 105 (53), 77 (38), 66 (13), 51 (11). Also isolated was acetophenone (yield 62%) whose spectral data were identical to those of an authentic sample.

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[14]) Contains ⩽ 10% 2'-cyclopentenyl isomer.

[15]) Contains *ca.* 15% 2'-cyclopentenyl isomer.

[16]) Contains *ca.* 40% 2'-cyclopentenyl isomer.

[17]) Contains *ca.* 30% 2'-cyclopentenyl isomer.

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