2-Substituted Bicyclo[3.2.1]oct-2-en-8-ones by Carbonylation of Cycloheptadiene-Derived Iron Carbonyl Complexes Bearing Alkyl–Allyl Subunits

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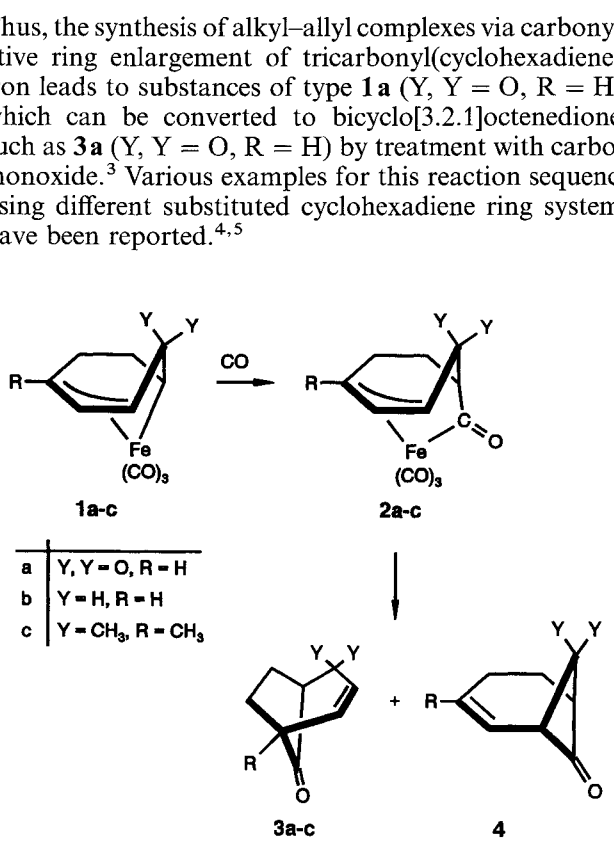
Iron carbonyl complexes **7**, generated by the reaction of cationic cycloheptadienyl complex **6** [L = $P(OPh)_3$] with appropriate nucleophiles, can be converted into bicyclooctenones **9** and **10** via carbonylative decomplexation. Treatment of **7** with CO (200 bar) at elevated temperatures yields the ketones **10** as the main products. Thus, carbonylation is accompanied by double bond migration.

Bicyclo[3.2.1]octenones can be generated by carbonylative decomplexation of iron carbonyl complexes with seven-membered-ring ligands bound to the metal in an alkyl–allyl fashion.[1–4] Various methods for the synthesis of the required starting materials are available.[5] These alternative pathways provide an approach to various interesting substrates bearing different substitution patterns and functionalities.

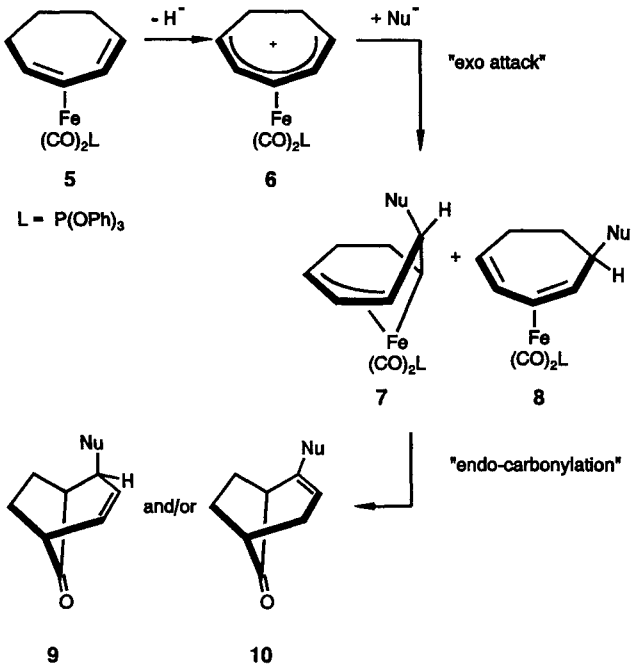
Thus, the synthesis of alkyl–allyl complexes via carbonylative ring enlargement of tricarbonyl(cyclohexadiene)-iron leads to substances of type **1a** (Y, Y = O, R = H), which can be converted to bicyclo[3.2.1]octenediones such as **3a** (Y, Y = O, R = H) by treatment with carbon monoxide.[3] Various examples for this reaction sequence using different substituted cyclohexadiene ring systems have been reported.[4,5]



Scheme 1

Another access to σ-alkyl–π-allyl bound seven-membered-ring complexes of iron starts from bicyclo[4.1.0]hept-2-ene systems.[6] The vinylcyclopropane subunit upon treatment with iron carbonyls is regioselectively attacked at the C(1)–C(6) bond to give the ring-opened product **1b** (Y = R = H) and **3b** upon further carbonylation. Similarly (+)-2-carene, containing a bicyclo[4.1.0]heptene skeleton gives the complex **1c** (Y = R = CH_3) and the bicyclooctenone **3c** without loss of optical activity.[7] The latter conversion (**1c** → **3c**) shows a stereospecific course of the ring-opening and carbonylation sequence. In some cases (e.g. **1c**) minor amounts of strained bicyclic systems of type **4** can be obtained. Alternatively decomplexation of **1c** by use of strongly oxidizing conditions offers an access to bicyclic lactones.[7]

Another efficient access to σ-alkyl–π-allyl complexes of type **1** is given by nucleophilic addition of hydrides and selected carbanions to η^5-cycloheptadienyl iron cations **6** [L = CO, $P(OPh)_3$] via attack of the internal C-2 atom in competition with the normal C-1 attack to form diene complex **8**.[1,8] Thus, reaction of tricarbonyl(cycloheptadienyl)iron with $NaBH_4$ gives a mixture of **7a** (Nu = H, L = CO) and **8a** (Nu = H, L = CO) in a 2:1 ratio.[1]



Scheme 2

The regioselectivity of the nucleophilic addition can be affected by the replacement of one CO ligand with weaker π-acceptor ligands such as PPh_3, $AsPh_3$ or $P(OPh)_3$.[9,10] Treatment of **6** (L = PPh_3) with $NaBH_4$ results in formation of **7a** (Nu = H, L = PPh_3) as the only product. Thus, contrary to the tricarbonyl complex **6** (L = CO), the use of such modified cycloheptadienyl salts **6** [L = PPh_3, $P(OPh)_3$] offers a regioselective approach to substituted alkyl–allyl complexes by the reaction with different carbon nucleophiles. In the conversions described above, the nucleophilic carbanion attack stereospecifically occurs '*trans*' to the iron carbonyl subunit and forms the *exo*-substituted compounds **7**.[10]

Hitherto the carbonylative decomplexation of substituted alkyl–allyl complexes obtained by this method has not been investigated and is only known for the conversion of the parent compound **7a** (Nu = H, L = CO) into **9a** or **10a**, respectively. In this paper, we report on the successful carbonylation of complexes of type **7** [L = $P(OPh)_3$]. Special attention is paid to the extent that the stereochemical information, introduced by the nucleophilic attack, can be transferred to the expected bicyclic ketones **9**. Our initial investigations have been focused on complexes of type **7** with L = $P(OPh)_3$, since the cycloheptadienyl salt **6** [L = $P(OPh)_3$] can be easily obtained in large scale preparations from cycloheptadiene.[10]

The conversion of **6** [L = $P(OPh)_3$] with RLi (R = Me, Bu, Ph) or NaCN at low temperatures leads to the known complexes **7b–d,i**.[10] Similarly the application of comparable nucleophiles offers access to alkyl–allyl compounds **7e–f**. Interestingly, lithiated alkynes also react with **6** [L = $P(OPh)_3$] in the described manner to give the complexes **7g–h** bearing alkyne substituents. The complexes **7b–h** are obtained in good yields; all conversions can be carried out in a 10–15 g scale. The resulting products are stable to air and moisture and can easily be stored and handled. The results are summarized in Table 1.

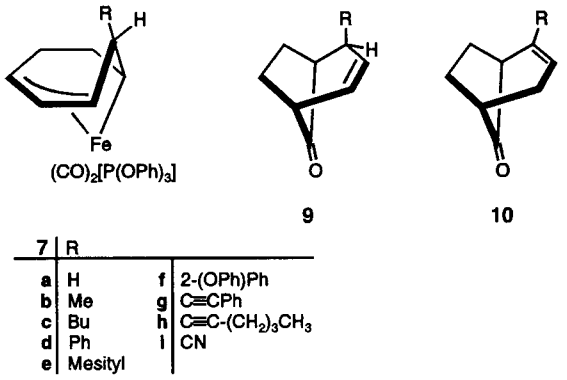
Table 1. Preparation of Alkyl–Allyl Complexes **7** [L = $P(OPh)_3$] by the Reaction of the Cycloheptadienyl Complex **6** with Nucleophiles

Reagent	Product	Yield (%)
MeLi	**7b**	94[10]
BuLi	**7c**	81[10]
PhLi	**7d**	77[10]
mesitylMgBr	**7e**	71
2-(OPh)PhLi	**7f**	57
PhC≡CLi	**7g**	67
$C_4H_9C{\equiv}CLi$	**7h**	81
NaCN	**7i**	60[10]

The carbonylative decomplexations of the alkyl–allyl complexes **7** were carried out in an autoclave at elevated temperatures under CO pressure (up to 200 bar). The reaction conditions were optimized in the case of **7d** [L = $P(OPh)_3$]. Heating of a dioxane solution of this substrate to 125 °C for 60 h under CO pressure (200 bar) gave the best yields of the carbonylation product **10d** (90 %) (Table 2).

Table 2. Influence of the Reaction Conditions on the Carbonylative Decomplexation of **7d** [L = $P(OPh)_3$] (T = 125 °C).

Solvent	CO Pressure (bar)	Time (h)	Yield **10d** (%)
benzene	80	48	39
benzene	100	216	50
benzene	200	48	47
dioxane	80	60	77
dioxane	200	60	90



7	R		
a	H	f	2-(OPh)Ph
b	Me	g	C≡CPh
c	Bu	h	C≡C-$(CH_2)_3CH_3$
d	Ph	i	CN
e	Mesityl		

Scheme 3

Under the conditions described above, the conversion of all complexes **7b–i** [L = $P(OPh)_3$] into bicyclo[3.2.1]octenones was achieved in good yields (54–90 %). The main products of these decomplexation reactions are the bicyclic ketones **10b–i**; only the reactions of **7b** and **7i** [L = $P(OPh)_3$] lead to mixtures of **10b** and **10i**, respectively, together with minor amounts of the ketones **9b** and **9i** (< 10 %). One significant exception from the observed product selectivity is the conversion of **7c** [L = $P(OPh)_3$], which yields a complex mixture of at least 4 isomeric bicyclic ketones in a 40:25:25:10 ratio (GC, GC-IR, GC-MS). Individual identification of single isomers and structural assignment was not possible in this case.

Table 3. Preparation of the Bicyclooctenones by Carbonylation of Complexes **7**

Educt	Ketones (ratio)	Yield (%)
7b	**10b** : **9b** (9 : 1)	61
7c	–[a]	40
7d	**10d**	90
7e	**10e**	68
7f	**10f**	60
7g	**10g**	78
7h	**10h**	54
7i	**10i** : **9i** (9 : 1)	61

[a] Mixture of four isomeric ketones, identification and structural assignments were not possible. Reaction carried out in benzene solution (125 °C, 80 bar CO pressure), yield not optimized.

The results of the carbonylation reactions, as summarized in Table 3, show the predominant formation of the bicyclic ketones **10**. Only small amounts of the expected ketones **9** were obtained. This is in line with mechanisms postulated for comparable reactions.[1] The carbonylative decomplexation is interpreted to proceed via CO insertion into the iron–alkyl unit followed by reductive elimination of the resulting acyl moiety with one carbon atom of the allyl unit. Hydrogen migration may occur via an allyl iron hydride species as postulated by Aumann.[1] Under the reaction conditions, this intermediate decomposes to give the ketones **9** and **10**, with predominance of the latter if thermodynamically controlled. The

more complex product mixture, obtained in the carbonylation of **7c**, can be explained as a result of subsequent hydrogen migrations along the butyl chain via different allyl iron hydride species. Possibly the unselective reaction course in this case can be influenced by modification of the reaction conditions.

Transformation of the compounds **7d–h** into corresponding bicyclooctenones **10d–h** as the sole products offers a new synthetic approach to these ketones. However, due to the double bond migration, the stereochemical information (*R-exo* relative to the metal), introduced in the synthesis of the complexes **7** under the conditions described above, cannot be transferred to the final decomplexation products. Due to the small yield of **9** in some carbonylation reactions, this reaction is not yet applicable to synthetic use. Further work to optimize the reaction conditions with respect to the formation of these compounds is necessary.

The high product selectivity during carbonylative decomplexations as reported above suggests the application of this method to the conversion of analogous alkyl–allyl complexes of type **7** bearing additional substituents. These can be derived from nucleophilic attack to substituted cycloheptadienyl salts.[12] This method should lead to bicyclic ketones bearing different substituents with predetermined position and geometry. Further investigations in this direction are in progress.

NMR spectra were recorded on Bruker spectrometers AC 200 and AM 300 with TMS as internal standard. IR spectra were obtained on a Shimadzu 470, mass spectra on a Finnigan CA 5 and elementary analysis on a Carlo Erba Mod 1106. Column chromatography was carried out with silica gel (70–230 mesh) from Merck, Darmstadt, by using MTBE (methyl *tert*-butyl ether)/PE (petroleum ether, bp 60–90 °C) mixtures as eluent; gas chromatography with 25 m or 50 m CP sil-5 capillaries. GC-MS and GC-IR spectra were obtained by using comparable capillaries and a Finnigan MAT 8320 (MS) and a Bruker IFS 48 (IR). The cycloheptadienyl iron salt **6** [L = $P(OPh)_3$] and the complexes **7b–d** and **7i** were prepared according to literature procedures.[10]

Dicarbonyl[3-5-η-1-σ-2-(2,4,6-trimethylphenyl)cycloheptadienyl](triphenylphosphite)iron (7e):
Under argon atmosphere, compound **6** (2.0 g, 3.3 mmol) was dissolved in THF (20 mL) and cooled to 0 °C. To this mixture, a solution of mesitylmagnesium bromide in THF (5 mL, c = 1 mol/L; 0.05 mmol) was added dropwise. After 10 min at this temperature and 10 min at 20 °C, Et_2O (20 mL) and water (15 mL) were added; the organic layer was separated, washed with water and dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the resulting residue (silica gel; PE/MTBE, 4:1) gave 1.5 g (71%) of **7e** as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.95 (m, 1H, H-7), 1.38 (m, 1H, H-7), 1.71 (m, 1H, H-1), 1.90 (m, 2H, H-6), 2.17 (s, 6H, CH_3), 2.50 (s, 3H, CH_3), 3.59 (t, 1H, H-4, ^3J = 7.0 Hz), 4.07 (t, 1H, H-2, ^3J = 7.7 Hz), 4.23 (t, 1H, H-5, ^3J = 7.7 Hz), 4.58 (m, 1H, H-3), 6.59 (s, 1H, H_{meta}), 6.69 (s, 1H, H_{meta}), 7.1–7.4 (m, 15H, PhH).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 14.0 (CH, C-1), 21.2 (CH_3), 24.6 (2 × CH_3), 26.6 (CH_2, C-7), 37.3 (CH_2, C-6), 49.2 (CH, C-2), 67.1 (CH, C_{Allyl}), 77.8 (CH, C_{Allyl}), 96.6 (CH, C_{Allyl}), 122–137 (C_{Ph}), 151.3 (*C*OP), 216 (C=O).

MS (EI, 70 eV): m/z (%) = 634 (1, M^+), 606 (16, $M^+ - CO$), 578 (18, $M^+ - 2CO$), 366 (80).

IR (KBr/film): ν = 1994 vs, 1938 vs, 1592 s, 1485 cm^{-1} s.

Dicarbonyl[3-5-η-1-σ-2-(2′-phenoxyphenyl)cycloheptadienyl](triphenylphosphite)iron (7f):
A solution of **6** (2.0 g, 3.3 mmol) in CH_2Cl_2 (20 mL) was cooled to − 78 °C and treated slowly with a solution of the lithiated reagent (1.4–1.5 equiv). The mixture was stirred for 15 min at this temperature and 15 min without cooling, and diluted with CH_2Cl_2 (10 mL). After MeOH (2 mL) and water (25 mL) were added, the organic layer was separated and washed with water (× 3). The yellow solution was dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification of the resulting residue was carried out by column chromatography (silica gel; PE/MTBE mixtures).

Diphenyl ether (1.6 g, 9.5 mmol) was lithiated by treatment with BuLi (3.2 mL, c = 1.6 mol/L in hexane, 5.1 mmol) in 10 mL THF at r.t.[13] Conversion of this mixture with the cycloheptadienyl salt **6** followed by chromatography (silica gel; PE/MTBE, 10:1) gave 1.3 g (57%) **7f** as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.95 (m, 1H, H-7), 1.30 (m, 1H, H-7), 1.70 (m, 3H, H-1, H-6), 3.21 (m, 1H, H-4), 4.10 (t, 1H, H-2, ^3J = 7.1 Hz), 4.24 (m, 1H, H-5), 4.65 (q, 1H, H-3, ^3J = 7.8 Hz), 6.9–7.3 (m, 24H, PhH).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 25.6 (d, CH, C-1, $^2J_{C-P}$ = 44.4 Hz), 26.6 (CH_2, C-7), 37.8 (CH_2, C-6), 46.2 (CH, C-2), 61.1 (CH, C_{Allyl}), 78.3 (CH, C_{Allyl}), 96.6 (CH, C_{Allyl}), 118–130 (C_{Ph}), 151.2 (d, *C*OP, $^2J_{C-P}$ = 6.4 Hz), 153.4 ($C_{Ph}OC_{Ph}$), 157.1 ($C_{Ph}OC_{Ph}$), 218.0 (CO).

MS (EI, 70 eV): m/z (%) = 656 (2, $M^+ - CO$), 628 (1, $M^+ - 2CO$).

IR (KBr/film): ν = 3070 m, 1997 vs, 1941 vs, 1592 s, 1450 cm^{-1} s.

Dicarbonyl[3-5-η-1-σ-2-(phenylethynyl)cycloheptadienyl](triphenylphosphite)iron (7g):
A solution of phenylacetylene (1.8 g, 18.3 mmol) in THF (20 mL) was cooled to − 78 °C and treated dropwise with BuLi (7.4 mL) in hexane (c = 1.6 mol/L, 11.8 mmol). The mixture was allowed to warm to r.t. and stirred for an additional 1 h. Reaction of this solution with **6** (4.0 g, 6.6 mmol) as described above and purification by chromatography (PE/MTBE, 5:1) and crystallisation from CH_2Cl_2/pentane yielded 2.75 g (68%) **7g** as yellow crystals (mp 128–129 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.28 (d, 1H, H-1, ^3J = 8.1 Hz), 1.85 (m, 2H), 1.98 (m, 1H), 2.09 (m, 1H), 3.23 (m, 1H, H-3), 3.60 (t, 1H, H-2, ^3J = 7.9 Hz), 4.35 (m, 2H, H-4, H-5), 7.1–7.3 (m, 20H, PhH).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 20.0 (d, CH, C-1, $^2J_{C-P}$ = 42.6 Hz), 26.5 (CH_2, C-7), 36.5 (CH, C-2), 39.1 (CH_2, C-6), 60.5 (CH, C_{Allyl}), 79.9 (CH, C_{Allyl}), 81.8 (C_q, $C_{Alkynyl}$), 91.8 (C_q, $C_{Alkynyl}$), 95.4 (CH, C_{Allyl}), 121.2 (CH), 123.7 (C_q, $C_{Ph}-C\equiv C$), 124.9 (CH), 127.5 (CH), 128.1 (CH), 129.7 (CH), 131.3 (CH), 151.1 (d, $C_{Ph}OP$, $^2J_{C-P}$ = 6.4 Hz), 217.3 (C=O), 217.6 (C=O).

MS (EI, 70 eV): m/z (%) = 616 (6, M^+), 588 (36, $M^+ - CO$), 561 (46, $M^+ - 2CO$–H].

IR (KBr/solid): ν = 1997 vs, 1937 vs, 1592 s, 1487 cm^{-1} s.

$C_{35}H_{29}FeO_5P$ (616.4): calc. C, 68.20; H, 4.74. Found C, 68.15; H, 4.75.

Dicarbonyl[3-5-η-1-σ-2-(hex-1-yn-1-yl)cycloheptadienyl](triphenylphosphite)iron (7h):
At − 78 °C a solution of BuLi (5 mL) in hexane (c = 1.6 mol/L, 8.0 mmol) was added dropwise to hex-1-yne (1.0 g, 8.3 mmol) in THF (10 mL). The mixture was swirled at this temperature for 15 min, and for a further 1 h without cooling. Treating the resulting solution as described above gave after chromatography (PE/MTBE, 4:1) 2.0 g (81%) **7h** as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.84 (t, 3H, CH_3, ^3J = 6.6 Hz), 1.0–1.3 (m, 5H), 1.6–2.0 (m, 4H), 2.05 (br s, 2H, CH_2-3′), 3.2 (br s, 1H, H-3), 3.36 (br s, 1H, H-2), 4.30 (br s, 2H, H-4, H-5), 7.1–7.4 (m, 15H, PhH).

^{13}C NMR (75.5 MHz, $CDCl_3$; 20 °C): δ = 13.5 (CH_3), 18.3 (CH_2), 20.3 (d, CH, C-1, $^2J_{PC}$ = 43.2 Hz), 21.8 (CH_2), 26.3 (CH_2), 31.1 (CH_2), 36.0 (CH, C-2), 38.9 (CH_2), 61.7 (CH, C_{Allyl}), 79.5 (CH, C_{Allyl}), 81.4 (C_q, C_{Alkyne}), 82.3 (C_q, C_{Alkyne}), 95.1 (CH, C_{Allyl}), 121.1

(CH, C_{Phenyl}), 124.8 (CH, C_{Phenyl}), 129.6 (CH, C_{Phenyl}), 151.1 (d, COP, $^2J_{PC}$ = 5.9 Hz), 217.4 (d, C=O, $^2J_{PC}$ = 7.7 Hz), 217.6 (d, C=O, $^2J_{PC}$ = 7.7 Hz).

IR (KBr/film): ν = 1995 vs, 1945 vs, 1592 s, 1485 cm^{-1} s.

2-Methylbicyclo[3.2.1]oct-2-en-8-one (10b) and 4-Methylbicyclo-[3.2.1]oct-2-ene-8-one (9b):

A solution of alkyl–allyl complex **7b** (7.0 g, 13 mmol) in dioxane (15 mL) was heated (120 °C) in an autoclave under a pressure (200 bar) of carbon monoxide for 60 h. The reaction mixture was filtered and the solvent removed in vacuo. Chromatography of the residue (silica gel; PE/MTBE, 5:1) gave a yellow fraction of iron complexes $[Fe(CO)_4P(OPh)_3]$. Changing the eluent to CH_2Cl_2 gave after evaporation of the solvent 1.1 g (61%) of bicyclic ketones as a colourless oil. This mixture consisted of **10b** and **9b** in a 8.5:1 ratio (^{1}H NMR) containing traces of another compound, presumably 2-*exo*-methylenebicyclo[3.2.1]octan-8-one. Further separation by column chromatography was not successful. The described products were identified by analysis of the NMR spectra of the mixture.

Compound **9b**:

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.04 (d, 3H, ^3J = 7.2 Hz), 1.7–2.1 (m, 4H, H-6, H-7), 2.21 (m, 1H), 2.48 (m, 1H), 3.11 (m, 1H, H-4), 5.33 (m, 1H), 5.74 (m, 1H).

Compound **10b**:

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.69 (q, 3H, CH_3, ^4J = 2 Hz), 1.7–2.3 (m, 6H, H-1, H-5, H-6, H-7), 2.35 (ddd, 1H, H-4, ^2J = 18.0, ^3J = 3.8, ^3J = 1.8 Hz), 2.76 (br d, 1H, H-4, ^2J = 18.0 Hz), 5.18 (t, 1H, H-3, ^3J = 1.7 Hz).

MS (mixture of **9b** and **10b**, EI, 70 eV): *m/z* (%) = 137 (90, $M^+ + 1$), 109 (100).

IR (mixture of **9b** and **10b**, KBr/film): ν = 2980 m, 1749 cm^{-1} vs.

Carbonylation of 7c:

A benzene solution of **7c** (1.5 g, 2.6 mmol) heated at 120 °C for 60 h at 80 bar CO, after workup similar as described above, yields 0.19 g (40%) of a slightly yellow oil, which consisted of a 10:25:40:25 mixture (GC) of isomeric bicyclic ketones [GC-MS: *m/z* = 179 ($M^+ + 1$). GC-IR: ν = 1760–1770 cm^{-1}. NMR spectra of the mixture showed resonances at the expected chemical shifts). Further attempts to separate these compounds using column chromatography did not give pure compounds. Structural assignments of the single isomers were not possible.

2-Phenylbicyclo[3.2.1]oct-2-en-8-one (10d):

The raw material, obtained from carbonylation of **7d** (2.0 g, 3.4 mmol) as described above, could be crystallized from CH_2Cl_2/pentane to give 0.60 g (90%) **10d**[11] as colourless crystals.

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ = 1.89 (m, 1H), 2.24 (m, 3H), 2.38 (m, 1H), 2.64 (ddd, 1H, H-4_{endo}, ^2J = 18.0, ^3J = 3.5, ^3J = 2.2 Hz), 3.0 (m, 2H, H-1, H-4_{exo}), 5.88 (t, 1H, H-3, ^3J = 3.5 Hz), 7.3 (m, 5H, PhH).

^{13}C NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 25.9 (CH_2, C-7), 30.3 (CH_2, C-6), 41.3 (CH_2, C-4), 42.0 (CH, C-5), 47.7 (CH, C-1), 121.2 (CH), 125.4 (CH), 127.4 (CH), 128.4 (CH), 139.2 (C_q, C-2), 143.8 (C_q, C_{Ph^-ipso}), 217.4 (C=O).

MS (EI, 70 eV): *m/z* (%) = 198 (100, M^+), 170 (78, M^+ – CO).

IR (KBr/solid): ν = 3040 w, 2970 m, 1754 cm^{-1} vs.

$C_{14}H_{14}O$ (198.3): calc. C, 84.81, H, 7.12. Found C, 84.90; H, 7.25.

2-(2,4,6-Trimethylphenyl)bicyclo[3.2.1]oct-2-en-8-one (10e):

Carbonylation of **7e** (1.5 g, 2.4 mmol) and workup as described above yielded 0.33 g (68%) of the title compound **10e** as a colourless oil.

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ = 2.00 (m, 2H), 2.18 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.2–2.4 (m, 3H), 2.46 (d, 1H, H-1, ^3J = 5.5 Hz), 2.64 (ddd, 1H, H-4_{endo}, ^2J = 18.0, ^3J = 3.2, ^3J = 2.2 Hz), 3.03 (br d, 1H, H-4_{exo}), 5.36 (t, 1H, H-3, ^3J = 3.2 Hz), 6.86 (s, 1H, PhH), 6.89 (s, 1H, PhH).

^{13}C NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 20.0 (CH_3), 20.5 (CH_3), 20.8 (CH_3), 26.0 (CH_2, C-7), 29.2 (CH_2), C-6), 41.8 (CH_2, C-4), 42.0 (CH, C-5), 50.5 (CH, C-1), 123.5 (CH, C-3), 128.1 (CH, C_{Ph^-meta}), 128.4 (CH, C_{Ph^-meta}), 134.8 (C_q), 136.1 (C_q), 136.4 (C_q), 137.5 (C_q), 142.9 (C_q), 217.5 (C=O).

MS (EI, 70 eV): *m/z* (%) = 240 (100, M^+), 225 (4, $M^+ - CH_3$), 212 (30, M^+ – CO).

IR (KBr/film): ν = 2975 m, 2920 m, 1750 vs, 1450 cm^{-1} m.

2-(2′-Phenoxyphenyl)bicyclo[3.2.1.]oct-2-en-8-one (10f):

Conversion of **7f** (1.20 g, 1.8 mmol) as described above and chromatography (silica gel; PE/MTBE, 7:1) gave as the second fraction 0.30 g (60%) **10f** as colourless crystals (mp 74–75 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.75 (m, 1H, H-6_{endo}), 2.00 (m, 2H, H-6_{exo}, H-7_{exo}), 2.35 (m, 2H, H-5, H-7_{endo}), 2.55 (ddd, 1H, H-4_{endo}, ^2J = 17.9 Hz, ^3J = 3.4 Hz, ^3J = 2.2 Hz), 2.80 (d, 1H, H-1, ^3J = 5.5 Hz), 2.91 (br d, 1H, H-4_{exo}), 5.73 (t, 1H, H-3, ^3J = 3.4 Hz), 6.9–7.3 (m, 9H, H_{Phenyl}).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 25.9 (CH_2, C-6), 30.2 (CH_2, C-7), 41.5 (CH_2, C-4), 42.0 (CH, C-5), 48.7 (CH, C-1), 117.9 (CH), 119.8 (CH), 122.7 (CH), 123.7 (CH), 124.4 (CH), 128.7 (CH), 129.6 (CH), 130.3 (CH), 132.7 (C_q, C-2), 142.0 (C_q, C_{ipso^-Ph}), 153.5 ($C_{Ph}OC_{Ph}$), 157.3 ($C_{Ph}OC_{Ph}$), 216.9 (C=O).

MS (EI, 70 eV): *m/z* (%) = 290 (100, M^+), 262 (30, M^+ – CO).

IR (KBr/solid): ν = 1754 vs, 1591 m, 1575 m, 1482 m, 1273 cm^{-1} vs.

$C_2OH_{18}O_2$ (290.4): calc. C, 82.73; H, 6.25. Found C, 82.65; H, 6.25.

2-(Phenylethynyl)bicyclo[3.2.1]oct-2-en-8-one (10g):

Reaction of **7g** (2.5 g, 4.3 mmol) with carbon monoxide followed by the usual workup (eluent: PE/MTBE, 5:1) and crystallization from CH_2Cl_2/pentane gave 0.70 g (78%) **10g** as colourless crystals (mp 62–63 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.85 (m, 1H, H-6_{endo}), 2.09 (m, 1H, H-7_{exo}), 2.16 (m, 1H, H-6_{exo}), 2.32 (m, 2H, H-5, H-7_{endo}), 2.57 (ddd, 1H, H-4_{endo}), 2.65 (d, 1H, H-1, ^3J = 5.6 Hz), 3.01 (br d, 1H, H-4_{exo}, ^2J = 18.7 Hz), 6.00 (t, 1H, H-3, ^3J = 3.6 Hz), 7.28 (m, 3H, H_{Phenyl}), 7.40 (m, 2H, H_{Phenyl}).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 25.3 (CH_2, C-6), 29.5 CH_2, C-7), 41.1 (CH_2, C-4), 41.2 (CH, C-5), 49.0 (CH, C-1), 87.7 (C_q, C_{Alkyne}), 87.8 (C_q, C_{Alkyne}), 122.6 (C_q, C_{ipso^-Ph}), 126.7 (C_q, C-2), 128.0 (CH, C_{Ph}), 130.9 (CH, C-3), 131.2 (CH, C_{Ph}), 214.6 (C=O).

MS (EI, 70 eV): *m/z* (%) = 222 (100, M^+), 194 (26, M^+ – CO).

(KBr/solid): ν = 2970 m, 1748 vs, 1488 m, 1444 cm^{-1} m.

$C_{16}H_{14}O$ (222.3): calc. C, 86.45; H, 6.35, Found C, 86.40; H, 6.40.

2-(Hex-1-yn-1-yl)bicyclo[3.2.1]oct-2-en-8-one (10h):

Conversion of **7h** (2.0 g, 3.4 mmol) and workup as above (PE/MTBE; 2:1) yielded 0.37 g (54%) **10h** as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.91 (t, 3H, CH_3, ^3J = 7.2 Hz), 1.4 (m, 4H), 1.81 (m, 1H), 2.05 (m, 2H), 2.3 (m, 3H, H-5, CH_2-3′), 2.50 (m, 2H, H-1, H-4_{endo}), 2.86 (br d, 1H, H-4_{exo}, ^2J = 18.8 Hz), 5.80 (t, 1H, H-3, ^3J = 3.6 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 13.6 (CH_3), 18.9 (CH_2), 22.0 (CH_2), 25.5 (CH_2), 29.6 (CH_2), 30.7 (CH_2), 41.0 (CH_2, C-4), 41.5 (CH, C-5), 49.6 (CH, C-1), 79.3 (C_q, C_{Alkyne}), 89.1 (C_q, C_{Alkyne}), 127.4 (C_q, C-2), 129.0 (CH, C-3), 215.6 (C=O).

MS (EI, 70 eV): *m/z* (%) = 203 (30, M^+), 185 (10, M^+ – CO).

IR (KBr/film): ν = 2965 m, 2935 m, 1753 cm^{-1} vs.

2-Cyanobicyclo[3.2.1.]oct-2-en-8-one (10i) and 4-Cyanobicyclo-[3.2.1]oct-2-en-8-one (9i):

Conversion of **7i** (2.0 g, 3.7 mmol) as above gave 0.33 g (61%) of carbonylation products **10i** and **9i** in a 9:1 ratio (GC). The products were identified by analysis of the NMR spectra of the mixture and comparison with related compounds.

Compound **9i**:

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 4.12 (ddd, 1H, H-4, ^3J = 3.5, ^3J = 2.9, ^4J = 2.6 Hz), 5.54 (ddd, 1H, H-3, ^3J = 9.2, ^3J = 2.9, ^4J = 1.3 Hz), 6.13 (ddd, 1H, H-2, ^3J = 9.2, ^3J = 6.8, ^4J = 2.6 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 21.5 (CH_2), 28.3 (CH_2), 43.7 (CH, C-4), 120.0 (CH), 136.1 (CH), 117.6 (C_q, CN). Other signals in these spectra are overlapped by the resonances of **10i**.

GC-MS (t_R 9.8 min): m/z (%) = 147 (10, M^+), 119 (20, $M^+ - CO$).

GC-IR (t_R 11.2 min): ν = 2966 w, 1778 cm^{-1} vs.

Compound **10i**:

^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.8–2.5 (m, 5 H), 2.67 (d, 1 H, H-1, ^3J = 5.9 Hz), 2.70 (ddd, 1 H, H-4$_{endo}$, ^2J = 18.7, ^3J = 4.1, ^3J = 2.4 Hz), 3.01 (br d, ^2J = 18.7 Hz), 6.52 (dd, 1 H, H-3, ^3J = 4.1, ^3J = 3.1 Hz).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 25.0 (CH_2, C-6), 29.4 (CH_2, C-7), 40.6 (CH, C-5), 41.5 (CH_2, C-4), 46.0 (CH, C-1), 116.4 (C_q), 117.2 (C_q), 142.3 (CH, C-3), 211.5 (C=O).

GC-MS (t_R 10.4 min): m/z (%) = 148 (40, $M^+ + 1$), 119 (45, $M^+ - CO$).

GC-IR (t_R 13.6 min): ν = 2980 w, 2915 w, 1782 vs, 1141 cm^{-1} m.

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