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Regioselective Synthesis of Substituted Bicyclo[3.2.1]oct-3-ene-2,8-diones via Double Carbonylation of 1,3-Cyclohexadienes

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Double carbonylation of 1,3-cyclohexadienes **1** is applied to the synthesis of substituted bicyclo[3.2.1]oct-3-ene-2,8-diones **4**. The Lewis acid mediated ring enlargement of substituted cyclohexadiene complexes **2** produces the cycloheptanone alkyl allyl complexes **3** with high regioselectivity. Substituted bicyclic diketones **4** are obtained in high yields by treating the complexes **3** with carbon monoxide under pressure or by oxidative decomposition. The two carbonylation steps can also be performed in a one-pot version.

Regioselektive Synthese von substituierten Bicyclo[3.2.1]oct-3-en-2,8-dionen durch doppelte Carbonylierung von 1,3-Cyclohexadienen

Die zweifache Carbonylierung von 1,3-Cyclohexadienen **1** wird zur Synthese substituierter Bicyclo[3.2.1]oct-3-en-2,8-dione **4** angewandt. Die durch Lewissäuren herbeigeführte Ringerweiterung substituierter Cyclohexadienkomplexe **2** ergibt die Cycloheptanon-Alkyl-Allyl-Komplexe **3** mit hoher Regioselektivität. Substituierte bicyclische Diketone **4** werden in hohen Ausbeuten durch Behandeln der Komplexe **3** mit Kohlenmonoxid unter Druck oder durch oxidative Aufspaltung erhalten. Die beiden Carbonylierungsschritte können auch in einer Eintopfversion durchgeführt werden.

The bicyclo[3.2.1]octane carbon skeleton is an important structural unit found in various types of terpenoid natural products[1]. Diverse biological and pharmacological activities were found with compounds of this type. Hence, numerous synthetical routes leading to bicyclooctane systems have been developed. Among these we find ring enlargement procedures of other bicyclic systems[2], intramolecular ring closure[3], cycloaddition or ring annelation of a second carbon unit[4], rearrangements[5], and partial cleavage of tricyclic precursors[6].

Alternatively to these methods a two-step double carbonylation of tricarbonyl(1,3-cyclohexadiene)iron complexes **2** yielding bicyclo[3.2.1]oct-3-ene-2,8-diones **4**, which was first observed by *Lewis* and coworkers[7], might offer an entirely new and facile access to this carbon skeleton.

In a previous paper[8] we have discussed regioselectivity and mechanism of the first carbonylation step of this reaction sequence. Here now we report on the

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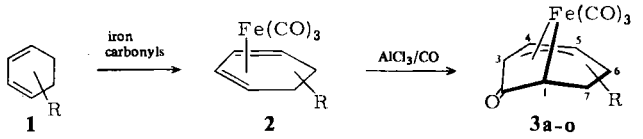
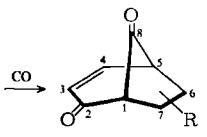
further carbonylation of the resulting complexes **3** producing variously substituted bicyclo[3.2.1]octenediones (type **4**) in high yields.





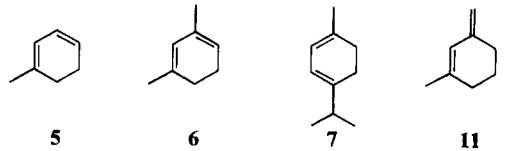
3, 4	Substituents	Yield 4
a	1-methyl	n.a.
b	5-methyl	not isolated
c	1,4-dimethyl	85%
d	3,5-dimethyl	not isolated
e	5-isopropyl-1-methyl	87%
f	6-isopropyl-3-methyl	n.a.
g	6,6,7,7-tetramethyl	67%
h	7,7-dimethyl	88%
i	1,6,6-trimethyl	84%
k	1,4,6,6-tetramethyl	97%
l	1,3,6,6-tetramethyl	69%
m	3,4,6,6-tetramethyl	81%
n	3,4,7,7-tetramethyl	77% (87%*)
o	3,7,7-trimethyl	see text

*) With $Ce(NH_4)_2(NO_3)_6$ at room temp.

Ring Enlargement of Further Cyclohexadiene Complexes 2

Ring enlargement products **3g–o** have already been described[8]. **3a, c, e, f** were obtained in an analogous manner from the corresponding dienes **5–7** via the tricarbonyliron complexes **8–10**.

Diene **5**[9] and its tricarbonyliron complex **8**, which had hitherto only been obtained in a mixture of isomers[10], were prepared free of isomers in a two-step procedure starting from 3-methyl-2-cyclohexen-1-one[11] analogous to known procedures of the Bamford-Stevens type elimination[12] and complexation with nonacarbonyldiiron under mild conditions.



Dienes:	**5**	**6**	**7**	**11**
$Fe(CO)_3$ Complexes	**8**	**9**	**10**	

The new tricarbonyliron complex **9** of 1,3-dimethyl-1,3-cyclohexadiene (**6**) was obtained also starting from 3-methyl-2-cyclohexen-1-one via Grignard addition and dehydration yielding a mixture of the isomeric dienes **6** and **11** in a 2:3 ratio[13].

Upon treatment of this diene mixture with $Fe(CO)_5$ (140°C, dibutyl ether) complex **9** was obtained free of isomers in 85% yield.

Complex **10**[14] of commercially available α-terpinene (**7**) has been prepared photochemically[14] in 52% or thermally analogous the above mentioned procedure in 80% yield.

According to our previous observations[8] complex **8** only gave ring enlargement product **3a** and not **3b** and similarly complex **9** formed solely **3c** and not **3d**. With the terpinene complex **10** the allyl-alkyl system **3e** was isolated as the main product (21%) while the side product **3f** (0.5%) obviously is due to minor isomerization of diene complex **10** under the reaction conditions. Indeed, recovered starting material also contained complexes of isomeric terpinenes.

The structures of the products obtained were determined by NMR, IR, mass spectra, and elementary analysis (or high resolution MS for **3f**) as well as comparison with the data of analogous compounds[8].

All conversions with aluminium chloride were performed according to the procedure of *Lewis* et al.[7] in methylene chloride at room temperature under atmospheric CO pressure, although much longer reaction times were required for sufficient conversion rates. If, however, CS_2 instead of CH_2Cl_2 was used as solvent, reaction at room temperature already came to an end after 2 h. In several cases conversion rates and yields were considerably higher while regioselectivity with unsymmetrical substrates was maintained. Thus, the diene complex **9** after 2 h reaction time at room temperature gave **3c** in 71% yield, while in CH_2Cl_2 after 12 d only 43% had been obtained. Reaction of the terpinene complex **10** in CS_2 after 2 h gave 44% of **3e** (instead of 21% after 14 d in CH_2Cl_2). No isomerization in the recovered starting material was observed and no ring-enlargement products of isomeric diene complexes such as **3f** were isolated. Instead, in 6% yield an oxidized ring enlargement product was isolated, which was assigned to structure **12** according to analytical and spectroscopical data. Up to now no mechanistic explanation of the oxidation in the isopropyl group to form a hydroxyl group can be offered.

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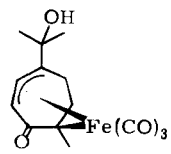


In all experiments a tenfold excess of $AlCl_3$ was applied. With less $AlCl_3$ yields dropped considerably. Also on lowering the temperature to 0°C only small amounts of ring enlargement products could be detected.

Formation of Bicyclo[3.2.1]oct-3-ene-2,8-diones 4

According to the observations of *Lewis* et al.[7] with the unsubstituted cyclohexadiene ring enlargement product **3** two conversions should be possible also with the substituted system described here: thermal isomerization to cyclohepta-

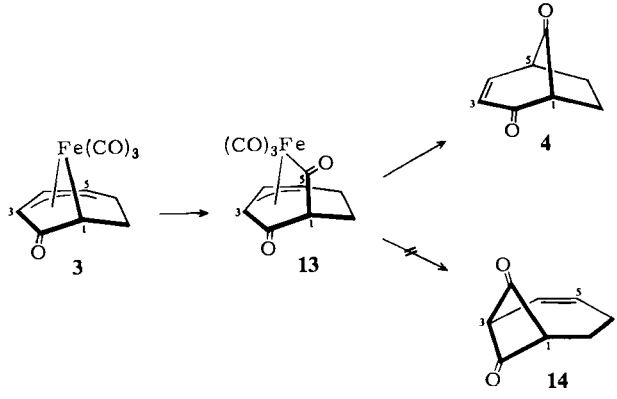
dienone complexes and further carbonylation to the bicyclo[3.2.1]octenedione skeleton **4**.

The first reaction might open a new access to the formation of substituted cycloheptane derivatives, which usually are not easily available[15], or possibly the hydroazulene skeleton[16] if hydroindane starting materials were used. Complexes of type **3** as obtained by us, however, in no case produced isomerized cycloheptadienones[8]. Blocking of the isomerization by quaternary centers in the ring presumably is responsible, but the systems **3a, c, e**, and **f**, too, showed no detectable tendency to form cyclohexadienone complexes.

Further carbonylation of complexes **3** with various substitution patterns (**3a–o**) to form the corresponding bicyclooctenediones **4a–o**, however, could be achieved in good to excellent yields if these complexes were heated to 120–140°C at 120–150 atm carbon monoxide pressure. All structures were assigned by analytical and spectroscopical data given in Table 2 (see Exp. Part). Oxidative decomposition, as was shown in one case (**3n**), also leads to the diketones **4**.

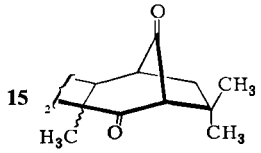
These results show that starting from substituted cyclohexadienes **1** via complexation, regioselective carbonylating ring enlargement, and further carbonylation the bicyclo[3.2.1]octane skeleton can be prepared with various substitution patterns. Even quaternary bridgehead carbons can be produced via carbonylation as is shown with product **3e** obtained from α-terpinene **7**. In usual carbonylations of olefins such as hydroformylation the formation of quaternary centers is unfavourable[17].

The reaction leading to the bicyclic diketones **4** may be interpreted as a two-step reaction (besides further ligand exchange steps). First migratory carbonyl insertion into the iron carbon bond (Fe–C-1) forms the acyl system **13**. Then via reductive elimination the acyl carbon is linked to C-5 to form the ketone bridge in **4**. Similar reactions have been observed with analogous complexes which, however, have been obtained by other reactions than described above[18]. Bridge formation between C-1 and C-5 is not the only possible orientation. Carbon atom C-3 of the allylic unit can also be the reaction center instead of C-5. In this case, as recently described[19] with a system similar to **3** (obtained from carvene), a bicyclic product of type **14** containing a four-membered ring is formed. While



there[19] the center C-2 is a methylene group, in our case C-2 carries the carbonyl group introduced in the carbonylating ring enlargement step. Bridging of C-1 and C-3 with a carbon monoxide unit to form **14** would separate the carbonyl group at C-2 and the new olefinic double bond by an sp^3 carbon, while in systems of type **4** these functions are in conjugation. In agreement with these arguments products of type **14** could not be detected in our case.

While usually good yields and no side products (such as systems analogous to **14**) were obtained in the reactions described, in one case (**3o**) an unexpected compound was obtained as the sole product. According to the mass spectrum a dimeric system was formed. NMR showed no signals of olefinic protons. Thus a structure of type **15** is suggested. Due to low resolution and unresolved NMR signals it is not clear, whether a product mixture or an unsymmetrical system of type **15** has been formed. Metal-induced [2 + 2] cycloadditions were observed in many cases[20]. With iron carbonyls, however, olefins (specially strained olefins) usually form cyclopentanones via additional carbonylation[21].



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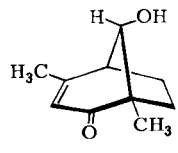

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The two-step conversion of cyclohexadiene complexes **2** to form the bicyclo[3.2.1]octane skeleton could also be performed in a one-pot version: **9** was first reacted with $AlCl_3$ under normal carbon monoxide pressure at room temperature in CS_2 in an autoclave. Without isolation of the ring enlargement product **3c**, higher temperatures and higher carbon monoxide pressure were applied leading directly to product **4c**. Yields were still rather low (20%) and have to be optimized. The side product **16** observed in this experiment in 11% yield also contains the bicyclo[3.2.1]octane skeleton. One of the carbonyl groups, however, had been selectively reduced to a hydroxy group. Whether this reduction is due to the formation of metal hydrides or hydrogen via water gas shift reaction[22] or via hydrogen transfer (e. g. from a cyclohexadiene unit to form an aromatic system, as observed in a similar case[23]) cannot be decided at present.

A one-pot version of this synthetic method would allow a shorter and easier reaction procedure. Therefore further investigations starting directly from the cyclohexadienes **1** to form bicyclo[3.2.1]octenediones **4** without isolation of any organometallic intermediates are under way.

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Experimental Part

Column chromatography: Alumina (Woelm, Eschwege, or Macherey, Nagel & Co., Düren, B = basic, S = acidic, 1–4 = activities) and Kieselgel 60 (70–230 mesh, Merck, Darmstadt). – Melting points: Tottoli melting point apparatus, Büchi, Flawil, not corrected. – IR spectra: Perkin Elmer 125 Infrarot Gitterspectrometer. – NMR: WM 300 NMR spectrometer (TMS internal standard, δ = 0.0 ppm). – Mass spectra: Varian MAT 311a (data system SS 100), direct inlet, EI = electron impact, 70 eV, FI = field ionization (molecular peaks based on ^{56}Fe).

1) *1-Methyl-1,3-cyclohexadiene* (**5**): A solution of 5.50 g (50 mmol) of 3-methyl-2-cyclohexen-1-one and 9.30 g (50 mmol) of tosylhydrazine in 50 ml of THF with 0.5 ml of conc. hydrochloric acid were heated to reflux for 6 h. After cooling 100 ml of benzene were added to the red reaction mixture. THF and benzene/water then were distilled off until the b.p. of pure benzene was reached. The residue then was cooled in an ice bath and 73 ml (0.11 mol) of a 1.5 M solution of *n*-butyllithium in hexane were added within 40 min. While stirring vigorously the mixture was carefully hydrolyzed with 100 ml of water. Extraction with three 100 ml portions of ether, drying of the combined organic layers over sodium sulfate, and fractionated distillation using a Vigreux column gave 1.05 g (22%) of **5**, b.p. 110°C (lit.[9] 108–110°C).

2) *Tricarbonyl[(1,2,3,4-η)-1-methyl-1,3-cyclohexadiene]iron* (**8**): While stirring 7.30 g (20 mmol) of nonacarbonyldiiron was added to a solution of 0.94 g (10 mmol) of **5** in 75 ml of benzene/THF (5:1). The mixture was stirred for 20 h at 40°C and then filtered through a small column of alumina (B 2–3). The column was washed with dry ether. Organic solvents were distilled off in vacuo. The residue was chromatographed on alumina (B 2–3). The main fraction of a kugelrohr distillation (oven temp. 40°C/0.05 Torr) gave 0.82 g (35%) of **8**[10]. According to NMR this sample was free of other isomers (<2%). – ^{1}H NMR ($CDCl_3$): δ = 1.60 (s, 3H, 1-CH_3), 1.70 (m, 4H, CH_2), 3.08 (m, 1H, 4-H), 5.10 (m, 2H, 2-, 3-H). – IR ($CHCl_3$): CO 2045(s), 1965(m) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 234 (M^+, 5%), 206(37), 178(9), 176(12), 148(100), 91(17), 56(70).

3) *1,3-Dimethyl-2-cyclohexen-1-ol:* A 2.0 g portion of 100.0 g (0.70 mol) of methyl iodide in 180 ml of absol. ether was added to a suspension of 17.0 g (0.70 mol) of magnesium turnings in 70 ml of absol. ether while stirring. After the Grignard formation has started the methyl iodide solution was added at a rate to maintain gentle reflux. After complete addition the mixture was heated to reflux for 1 h. Then while cooling to 0°C 55.0 g (0.56 mol) of 3-methyl-2-cyclohexen-1-one in 55 ml of absol. ether was added dropwise. After 4 h reflux the reaction mixture was cooled again and poured on 1500 g of ice. Ammonium chloride was added under stirring until the gelatinous mixture became homogeneous. The organic layer was separated and the aqueous residue extracted with three portions of 300 ml of ether. The combined organic layers were dried over sodium sulfate and the solvents were evaporated in vacuo. The residue after distillation gave 49.0 g (78%) of 1,3-dimethyl-2-cyclohexen-1-ol[13], b.p. 67°C/12 Torr (lit.[13] no comment on yields, b.p. 68°C/5 Torr). – ^{1}H NMR ($CDCl_3$): δ = 1.20 (s, 3H, 1-CH_3), 1.65 (s, br., 3H, 3-CH_3), 1.70 (m, 6H, CH_2), 2.05 (s, 1H, OH), 5.35 (s, br., 1H, 2-H).

4) *1,3-Dimethyl-1,3-cyclohexadiene* (**6**) *and 1-Methyl-3-methylene-1-cyclohexene* (**11**): Perchloric acid (250 ml, 5%) was added to a solution of 30.0 g (0.24 mol) of 1,3-dimethyl-2-cyclohexen-1-ol in 250 ml of ether. The reaction mixture was stirred vigorously for 30 min. After separation of the ether layer the aqueous phase was extracted with three 100 ml portions of ether. The combined ether extractions were washed neutral with water and dried

over sodium sulfate. Evaporation of solvents in vacuo and distillation gave 20.0 g (77%) of a 2:3 mixture of dienes **6** and **11**[13], b.p. 27°C/12 Torr (lit.[13] no comments on yield and b.p.). – ^{1}H NMR ($CDCl_3$) of the mixture: δ = 1.77 (m, 1- and 3-CH_3 of **6**, and 1-CH_3 of **11**), 2.05–2.40 (m, CH_2 of **6** and **11**), 4.62 (s, C=CH_2 of **11**), 5.32 (m, 4-H of **6**), 5.53 (m, 2-H of **6**), 5.95 (m, 2-H of **11**); ratio **6**:**11** = 40:60.

5) *Tricarbonyl[(1,2,3,4-η)-1,3-dimethyl-1,3-cyclohexadiene]iron* (**9**): A solution of a 2:3 mixture of dienes **6** and **11** (15.1 g, 0.14 mol) and 41.2 g (0.21 mol) of $Fe(CO)_5$ in 200 ml of absol. di-*n*-butyl ether was heated to reflux (140°C) for 60 h. After cooling the reaction mixture was filtered through a layer of alumina (B 2–3) under nitrogen. The alumina was washed with ether and the combined solutions were evaporated in vacuo condensing solvents, pentacarbonyliron, and unreacted dienes in a cooling trap. The oily residue was chromatographed on alumina (B 2–3) with hexane. The yellow main fraction upon distillation gave 29.6 g (85%) of **9**, b.p. 44°C/0.05 Torr. According to NMR the sample was (<2%) free of isomers. – ^{1}H NMR ($CDCl_3$): δ = 1.61 (s, 3H, 1-CH_3), 1.68 (m, 4H, CH_2), 2.06 (s, 3H, 3-CH_3), 3.10 (m, 1H, 4-H), 5.18 (s, br., 1H, 2-H). – IR ($CHCl_3$): CO 2040(s), 1962(m) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 248 (4%, M^+), 220(28), 190(15), 162(100), 160(10), 105(12), 91(16), 56(64).

$C_{11}H_{12}FeO_3$ (248.1) Calcd. C 53.26 H 4.88 Found C 53.45 H 4.81
Mol. weight 248 (M^+)

6) *Tricarbonyl[(1,2,3,4-η)-1-isopropyl-4-methyl-1,3-cyclohexadiene]iron* (**10**): A solution of 28.0 g (0.25 mol) of **7** and 49.0 g (0.25 mol) of $Fe(CO)_5$ in 400 ml of absol. benzene was irradiated under nitrogen for 3 d (TQ 150, Original Hanau, high pressure mercury lamp, 135 W, water cooling, duran glass filter). The mixture was filtered through a layer of alumina (B 2–3) under nitrogen. The alumina was washed with hexane and the combined organic solutions were evaporated in vacuo (solvent and $Fe(CO)_5$ were condensed in a cooling trap). Fractionated distillation of the residue gave 3.3 g (12%) of unreacted **7** (b.p. 57°C/15 Torr) and 29.4 g (52%) of **10**[14] as a yellow oil, b.p. 57°C/0.05 Torr (lit.[14] no comments on yields and b.p.).

Alternatively **10** could also be prepared in 80% yield when heating 6.8 g (50 mmol) of **7** and 36.4 g (0.10 mol) of $Fe_2(CO)_9$ in 250 ml of benzene/THF (5:1) for 20 h at 40°C. The reaction mixture was worked up as in the above procedure. – ^{1}H NMR ($CDCl_3$): δ = 1.05 (d, *J* = 7.0 Hz, 3H, isopropyl-CH_3), 1.10 (d, *J* = 7.0 Hz, 3H, isopropyl-CH_3), 1.53 (s, 3H, CH_3), 1.30–2.05 (m, 5H, tert. isopropyl-H and CH_2), 5.05 (s, 2H, 2- and 3-H). – IR ($CHCl_3$): CO 2040(s), 1955 (s, br.) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 276 (3%, M^+), 248(20), 218(18), 190(100), 174(31), 56(19).

7) *Ring Enlargement of* **8** *to Tricarbonyl[(1,3,4,5-η)-1-methyl-2-oxo-4-cycloheptene-1,3-diyl]iron* (**3a**): Under carbon monoxide atmosphere 4.0 g (30 mmol) of fresh, finely powdered $AlCl_3$ was suspended in 40 ml of CH_2Cl_2. After addition of 0.70 g (30 mmol) of **8** the suspension was stirred for 10 d at room temperature. The reaction mixture then was carefully poured on ice and extracted with three 50 ml portions of ether. After the combined organic layers were dried over sodium sulfate the solvents were evaporated in vacuo. The brown oily residue was chromatographed on silica gel. From the first yellow fraction eluated with hexane 0.36 g (46%) of the starting material was recovered. The second fraction, eluated with ether/methanol (10:1), gave after recrystallization from hexane 0.18 g (22%) of **3a** as yellow crystals, m.p. 105°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 3H, 1-CH_3), 1.66 (m, 2H, *exo*-6-H, *exo*-7-H), 2.27 (m, 2H, *endo*-6-H, *endo*-7-H), 4.37 (dd, *J* = 7.5/8.0 Hz, 1H, 4-H), 5.44 (dd, *J* = 8.0/8.0 Hz, 1H, 5-H), 5.80 (d, *J* = 7.5 Hz, 1H, 3-H). – IR ($CHCl_3$): CO 2080(s),

2020(s), 1590 (s, br.) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 262 (13%, M^+), 234(6), 206(46), 178(34), 176(23), 148(100), 56(89).

$C_{11}H_{10}FeO_4$ (262.0) Calcd. C 50.42 H 3.85 Found C 50.42 H 4.03
Mol. weight 262 (M^+)

8) *Ring Enlargement of* **9** *to Tricarbonyl[(1,3,4,5-η)-1,4-dimethyl-2-oxo-4-cycloheptene-1,4-diyl]iron* (**3c**): As described above a suspension of 36.7 g (0.275 mol) of $AlCl_3$ and 6.8 g (27.5 mmol) of **9** in 100 ml of CH_2Cl_2 was stirred for 12 d. Workup and chromatography on silica gel gave 2.5 g (36%) of the starting material and 3.3 g (43%) of **3c** as yellow crystals, m.p. 88°C. – ^1H NMR ($CDCl_3$): δ = 1.62 (s, 3H, 1-CH_3), 1.64 (m, 2H, *exo*-6-H, *exo*-7-H), 2.12 (s, 3H, 4-CH_3), 2.28 (m, 2H, *endo*-6-H, *endo*-7-H), 4.18 (ddd, *J* = 8.0/2.0/2.0 Hz, 1H, 5-H), 5.63 (d, *J* = 2.0 Hz, 1H, 3-H). – IR ($CHCl_3$): CO 2075(s), 2000(m), 1585 (s, br.) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 276 (7%, M^+), 248(5), 220(53), 192(35), 190(25), 176(18), 162(100), 91(33), 56(75).

$C_{12}H_{12}FeO_4$ (276.1) Calcd. C 52.21 H 4.38 Found C 52.27 H 4.30
Mol. weight 276 (M^+)

9) *Ring Enlargement of* **10** *to Tricarbonyl[(1,3,4,5-η)-6-isopropyl-3-methyl-2-oxo-4-cycloheptene-1,3-diyl]iron* (**3f**) *and Tricarbonyl[(1,3,4,5-η)-5-isopropyl-1-methyl-2-oxo-4-cycloheptene-1,3-diyl]iron* (**3e**): As described above a suspension of 60.0 g (0.45 mol) of $AlCl_3$ and 17.4 g (62.9 mmol) of **10** in 120 ml of CH_2Cl_2 was stirred for 14 d. Workup and chromatography on silica gel gave 3.2 g (18%) of the starting material (containing other isomers according to NMR) from the first fraction eluated with hexane. A second fraction eluated with hexane/ether (1:1) gave 0.1 g (0.5%) of **3f** as yellow oil, which was purified by further chromatography on silica gel with ether. A third fraction eluated with ether gave after recrystallization from hexane 5.85 g (21%) of **3e** as yellow crystals, m.p. 64°C.

3f: ^1H NMR ($CDCl_3$): δ = 0.81 (d; *J* = 6.5 Hz, 3H, isopropyl-CH_3), 0.91 (d, *J* = 6.5 Hz, 3H, isopropyl-CH_3), 1.30–1.45 (m, 2H), 2.10–2.25 (m, 1H), 2.25 (s, 3H, 3-CH_3), 2.60 (m, 1H, tert. isopropyl-CH), 2.88 (≈d, *J* = 7.2 Hz, 1H, 1-H), 4.13 (dd, *J* = 9.5/5.5 Hz, 1H, 5-H), 5.41 (d, *J* = 9.5 Hz, 1H, 4-H). – IR ($CHCl_3$): CO 2070(s), 2010(m), 1590 (s, br.) cm^{-1}. – UV (*n*-hexane): λ_{max} = 270, 314 nm. – MS (EI): *m/z* (rel. int.) = 304 (14%, M^+), 276(3), 248(98), 220(100), 204(25), 56(100).

$C_{14}H_{16}FeO_4$ (304.1) Calcd. 304.03932 Found 304.0393

3e: ^1H NMR ($CDCl_3$): δ = 1.19 (d, *J* = 6.5 Hz, 3H, isopropyl-CH_3), 1.29 (d, *J* = 6.5 Hz, 3H, isopropyl-CH_3), 1.30–1.45 (m, 1H), 1.59 (s, 3H, 1-CH_3), 1.80–2.00 (m, 2H), 2.14 (≈t, 1H), 2.30–2.45 (m, 1H), 5.39 (d, *J* = 7.0 Hz, 1H, 4-H), 5.53 (d, *J* = 7.0 Hz, 1H, 3-H). – IR ($CHCl_3$): 2063 (s), 2002 (m), 1587 (s, br.) cm^{-1}. – UV (*n*-hexane): λ_{max} (lg ε) = 273 (3.74), 320(3.39) nm. – MS (EI): *m/z* (rel. int.) = 304 (12%, M^+), 276(9), 248(54), 220(76), 204(18), 190(54), 56(100).

$C_{14}H_{16}FeO_4$ (304.1) Calcd. C 55.29 H 5.30 Found C 54.99 H 5.36
Mol. weight 304 (M^+)

10) *Ring Enlargement of* **9** *in CS_2 as Solvent:* Under argon a suspension of 6.7 g (50.0 mmol) of anhydrous powdered $AlCl_3$ in 50 ml of absol. CS_2 under vigorous stirring was cooled in an ice bath. Argon was replaced by a slow carbon monoxide stream and 1.25 g (5.0 mmol) of **9** was added. The cooling bath was withdrawn and after stirring the mixture for 2 h at room temp. it was cooled again in an ice bath, 50 ml of ether were added and this mixture was slowly poured on ice. The organic layer was separated and the aqueous solution extracted with three 100 ml portions of ether. After the combined organic phases

were dried over sodium sulfate the solvent was evaporated and the residue chromatographed on silica gel. Besides unreacted starting material in the less polar fraction eluated with hexane, a second yellow fraction eluated with methanol/ether (10:1) gave after further chromatography over a short column of silica gel 0.98 g (71%) of pure crystalline **3c**, m. p. 87°C.

When only a fivefold excess of $AlCl_3$ was used under the same conditions, yields dropped to 26%. When the reaction mixture with a tenfold excess $AlCl_3$ was kept at 0°C over the whole reaction period, nearly no conversion took place (5% **3c**) and 85% of the starting material was recovered.

11) *Ring Enlargement of* **10** *in* CS_2: A mixture of 13.3 g (0.10 mol) of anhydrous powdered $AlCl_3$ in 60 ml of CS_2 was stirred under carbon monoxide and 2.8 g (10.0 mmol) of **10** was added. After 2 h stirring at room temp. the mixture was cooled in an ice bath, 50 ml of ether was added and it was hydrolyzed with ice/water. The organic layer was separated and the aqueous phase extracted with three 100 ml portions of ether. The combined organic layers were dried over sodium sulfate, the solvent was evaporated in vacuo and the resulting brown oil was chromatographed on silica gel. Besides minor fractions of less stable products the main fraction eluated with ether contained 1.32 g (44%) of **3e** and the last fraction eluated with ether gave after recrystallization from hexane 180 mg (6%) of *tricarbonyl-[(1,3,4,5-η)-5-(1-hydroxy-1-methylethyl)-1-methyl-2-oxo-4-cycloheptene-1,3-diyl]iron* (**12**) as light yellow crystals, m.p. 142°C.

12: ^{1}H NMR ($CDCl_3$): δ = 1.32 (m, 1H), 1.50 (s, 3H, CH_3), 1.61 (s, 6H, CH_3), 1.92 (m, 2H), 2.46 (m, 1H), 2.66 (s, 1H, OH), 5.56 (d, J = 7.5 Hz, 1H, allylic H), 5.91 (d, J = 7.5 Hz, 1H, allylic H). – IR ($CHCl_3$): 3600–3100 (br.), 2080(s), 2000(m), 1590 (br.) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 320 (2%, M^+), 292(14), 264(28), 236(59), 218(78), 164(74), 149(100), 121(48), 107(41), 93(50), 91(45), 79(59).

$C_{14}H_{16}FeO_4$ (320.1) Calcd. C 52.53 H 5.04 Found C 52.33 H 5.11
Mol. weight 320 (M^+)

Table 1. Experimental data for the preparation of the bicyclooctenediones **4**

Starting material (g)		Product (g)		Yield %	M.p. °C	Kugelrohr Temp. °C/Torr
3c	(2.1)	**4c**	(1.04)	85	88	
3e	(2.0)	**4e**	(1.10)	87	–	70–74/0.15
3g	(1.0)	**4g**	(0.42)	67	198	–
3h	(0.9)	**4h**	(0.47)	88	88	–
3i	(2.6)	**4i**	(1.37)	84	89	–
3k	(1.0)	**4k**	(0.61)	97	39	110/0.3
3l	(0.5)	**4l**	(0.21)	69	–	84/0.4
3m	(0.4)	**4m**	(0.21)	81	38	
3n	(1.0)	**4n**	(0.49)	77	49	

12) *Carbonylating Decomplexation of Bicyclo[3.2.1]oct-3-ene-2,8-diones* **4** *from Complexes* **3** (*General Procedure*): In a 500 ml autoclave a solution of **3** (amounts given in Table 1) in 100 ml of absol. hexane was stirred at 120°C under 130 atm carbon monoxide pressure for 18 h. The reaction mixture then was filtered over a short column of silica gel, which afterwards was washed with several portions of ether. Solvent and pentacarbonyliron were

evaporated in vacuo and condensed in a cooling trap. The residue gave the raw diketones **4** as colourless to yellow oils. The crystalline products were recrystallized from hexane, all others distilled in a kugelrohr apparatus. For results see Table 1. Analytical and spectroscopical data of the compounds obtained are compiled in Table 2.

Table 2. Spectroscopical data of compounds **4**

Analysis	^{1}H NMR ($CDCl_3$) δ(ppm)	IR (Solvent) (cm^{-1})	Mass spectra (main fragm.) *m/z* (rel. int.)
1,4-Dimethylbicyclo[3.2.1]oct-3-ene-2,8-dione (4c)			
$C_{10}H_{12}O_2$ (164.2)	1.27 (s, 3H, 1-CH_3),	($CHCl_3$)	164 (40, M^+),
Calcd. C 73.15 H 7.37	1.78 (m, 1H, CH_2),	3020 m	149(2), 136(5),
Found C 73.19 H 7.42	1.94 (m, 2H, CH_2),	2985 m	121(5), 108(4),
	2.16 (d, J = 1.5 Hz, 3H, 4-CH_3),	2945 m	95(100), 69(10),
	2.26 (m, 1H, *endo*-6-H),	2885 m	67(26), 41(31),
	3.07 (d, J = 6.5 Hz, 5-H),	1760 m	39(20)
	6.05 (s, br., 1H, 3-H)	1670 m	
		1620 s	
5-Isopropyl-1-methylbicyclo[3.2.1]oct-3-ene-2,8-dione (4e)			
$C_{12}H_{16}O_2$ (192.3)	1.07 (2 d, J = 6.5 Hz,	($CHCl_3$)	192 (17, M^+),
Calcd. C 74.97 H 8.39	6H, isopr.-CH_3),	3020 m	164(19), 150(48),
Found C 74.99 H 8.35	1.27 (s, 3H, 1-CH_3),	2965 s	149(100), 121(51)
	1.80–2.32 (m, 5H, CH_2-6 and -7,	2940 s	
	isopr.-CH),	2878 m	
	6.30 (d, J = 9.5 Hz, 1H, 3-H),	1755 s	
	7.38 (d, J = 9.5 Hz, 1H, 4-H)	1675 s	
		1594 m	
6,6,7,7-Tetramethylbicyclo[3.2.1]oct-3-ene-2,8-dione (4g)			
$C_{12}H_{16}O_2$ (192.3)	1.02 (s, 3H, CH_3),	($CHCl_3$)	192 (20, M^+),
Calcd. C 74.97 H 8.39	1.10 (s, 3H, CH_3),	3020 w	177(15), 149(20),
Found C 74.91 H 8.28	1.13 (s, 3H, CH_3),	2990 m	110(33), 109(41),
	1.16 (s, 3H, CH_3),	2970 m	83(100)
	2.88 (dd, J = 8.0/2.0 Hz, 1H, 5-H),	1760 s	
	3.14 (≈s, 1H, 1-H),	1738 m	
	6.34 (dd, J = 9.5/1.5 Hz, 1H, 3-H),	1670 s	
	7.37 (dd, J = 9.5/8.0 Hz, 1H, 4-H)	1610 m	
7,7-Dimethylbicyclo[3.2.1]oct-3-ene-2,8-dione (4h)			
$C_{10}H_{12}O_2$ (164.2)	1.10 (s, 3H, *endo*-7-CH_3),	($CHCl_3$)	164 (28, M^+),
Calcd. C 73.15 H 7.37	1.17 (s, 3H, *exo*-7-CH_3),	3030 m	149(30), 83(100)
Found C 73.12 H 7.45	1.68 (d, J = 13 Hz, 1H, *endo*-6-H),	2975 m	
	2.04 (dd, J = 13/7.0 Hz, 1H,	2880 w	
	exo-6-H),	1770 s	
	3.13 (≈s, 1H, 1-H),	1758 s	
	3.25 (≈t, 1H, 5-H),	1672 s	
	6.22 (dd, J = 9.5/1.5 Hz, 1H, 3-H),	1595 m	
	7.57 (dd, J = 9.5/8.0 Hz, 1H, 4-H)		
1,6,6-Trimethylbicyclo[3.2.1]oct-3-ene-2,8-dione (4i)			
$C_{11}H_{14}O_2$ (178.2)	1.12 (s, 3H, *endo*-6-CH_3),	($CHCl_3$)	178 (32, M^+),
Calcd. C 74.13 H 7.92	1.16 (s, 3H, *exo*-6-CH_3),	3025 m	163(9), 150(159),
Found C 74.24 H 8.01	1.30 (s, 3H, 1-CH_3),	2970 m	135(33), 109(51),
	1.72 (≈s, 2H, *exo*- and	2940 m	107(23), 81(47),
	endo-7-H),	2875 m	40(67), 38(100)
	2.95 (d, J = 7.5 Hz, 1H, 5-H),	1762 s	
	6.31 (d, J = 9.5 Hz, 1H, 3-H),	1675 s	
	7.30 (d, J = 9.5/7.5 Hz, 1H, 4-H)	1595 w	

Table 2 (*Continued*)

1,4,6,6-Tetramethylbicyclo[3.2.1]oct-3-ene-2,8-dione (**4k**)			
$C_{12}H_{16}O_2$ (192.3)	1.10 (s, 3H, *endo*-6-CH_3),	($CHCl_3$)	192 (100, M^+),
Calcd. C 74.97 H 8.39	1.15 (s, 3H, *exo*-6-CH_3),	2975 m	177(43), 164(35),
Found C 74.69 H 8.34	1.26 (s, 3H, 1-CH_3),	2940 m	149(100), 95(95)
	1.64 (d, J = 14 Hz, 1H, *endo*-7-H),	2880 w	
	1.74 (d, J = 14 Hz, *exo*-7-H),	1760 s	
	2.13 (d, J = 1.5 Hz, 3H, 4-CH_3),	1668 s	
	2.72 (s, 1H, 5-H),	1619 m	
	6.09 (≈s, 1H, 3-H)		
1,3,6,6-Tetramethylbicyclo[3.2.1]oct-3-ene-2,8-dione (**4l**)			
$C_{12}H_{16}O_2$ (192.3)	1.06 (s, 3H, *endo*-6-CH_3),	($CHCl_3$)	192 (100, M^+),
Calcd. C 74.97 H 8.39	1.12 (s, 3H, *exo*-6-CH_3),	3020 m	177(40), 164(15),
Found C 74.83 H 8.35	1.29 (s, 3H, 1-CH_3),	2965 s	149(53), 123(33),
	1.64 (s, br., 2H, *exo*- and	2938 s	95(24)
	endo-7-H),	2875 m	
	1.88 (d, J = 1.5 Hz, 3H, 3-CH_3),	1760 s	
	2.87 (d, J = 8.0 Hz, 1H, 5-H),	1672 s	
	7.05 (dd, J = 1.5/8.0 Hz, 1H, 4-H)	1620 m	
3,4,6,6-Tetramethylbicyclo[3.2.1]oct-3-ene-2,8-dione (**4m**)			
$C_{12}H_{16}O_2$ (192.3)	1.07 (s, 3H, *endo*-6-CH_3),	($CHCl_3$)	192 (100, M^+),
Calcd. C 74.97 H 8.39	1.16 (s, 3H, *exo*-6-CH_3),	3020 m	177(43), 164(41),
Found C 74.98 H 8.46	1.33 (d, J = 13.6 Hz, 1H, *endo*-7-H),	2965 m	149(83), 109(60)
	1.85 (s, 3H, 3- or 4-CH_3),	2875 w	
	2.06 (dd, J = 13.6/7.8 Hz, 1H,	1760 s	
	exo-7-H),	1745 s	
	2.12 (s, 3H, 3- or 4-CH_3),	1665 s	
	2.69 (d, J = 1.9 Hz, 1H, 5-H),	1610 m	
	3.41 (dd, J = 7.8/1.9 Hz, 1H, 1-H)		
3,4,7,7-Tetramethylbicyclo[3.2.1]oct-3-ene-2,8-dione (**4n**)			
$C_{12}H_{16}O_2$ (192.3)	1.01 (s, 3H, *endo*-7-CH_3),	($CHCl_3$)	192 (22, M^+),
Calcd. C 74.97 H 8.39	1.15 (s, 3H, *exo*-7-CH_3),	3025 m	177(55), 149(14),
Found C 74.80 H 8.46	1.55 (d, J = 13 Hz, *endo*-6-H),	2970 s	109(57), 83(100)
	1.80 (s, 3H, 3- or 4-CH_3),	2945 m	
	2.02 (dd, J = 13.0/7.0 Hz,	2880 m	
	1H, *exo*-6-H),	1775 s	
	2.15 (3H, 3- or 4-CH_3),	1750 s	
	3.02 (dd, J = 1.8/7.0 Hz, 1H, 5-H),	1660 s	
	3.08 (d, J = 1.8 Hz, 1H, 1-H)	1618 s	

13) *Carbonylating Decomposition of* **3o** *to Form* **15**: When 1.5 g (5.2 mmol) of **3o** in 140 ml of absol. hexane was treated in an autoclave under carbon monoxide pressure (125°C, 150 atm, 18 h) workup as described above gave 0.90 g (93%) of the dimeric product **15** as colourless crystals, m.p. 151°C. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, CH_3), 1.09 (s, CH_3), 1.11 (s, CH_3), 1.16 (s, CH_3), 1.40–2.68 (m). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (t), 25.5, 26.4, 28.3 (q), 29.5 (q), 31.7 (q), 35.4 (s), 40.3, 40.7, 41.5, 42.1, 42.8, 44.1, 44.2, 59.0 (d), 69.0 (d), 76.5 (s), 103.1 (s), 143.0 (s), 201.7 (s), 206.3 (s), 219.9 (s). – IR ($CHCl_3$): 3020, 2965, 2937, 2875, 2840, 1754, 1740, 1675 cm^{-1}. – MS (FI): m/z = 356 (M^+). – MS (EI): m/z (rel. int.) = 356 (59%, M^+), 341(6), 328(5), 313(54), 179(56), 163(100), 135(47), 83(62), 55(66), 41(90).

$C_{22}H_{28}O_4$ (356.5) Calcd. C 74.12 H 7.92 Found C 74.22 H 8.05
Mol. weight 356 (M^+)

14) *Oxidative Decomposition of* **3n** *to Form* **4n**: Under nitrogen a mixture of 0.30 g (1.0 mmol) of **3n**, 20 ml of water, and 1.1 g (2.0 mmol) of $Ce(NH_4)_2(NO_3)_6$ was stirred for

6 h at room temperature. The reaction mixture then was extracted with three 10 ml portions of ether. The combined ether extractions were washed with water, dried over sodium sulfate, and evaporated in vacuo. The residue was chromatographed on silica gel with ether to yield 0.20 g (87%) of **4n** as a colourless oil, which on standing crystallized, m.p. 49°C.

15) *One-pot Version of Preparation of* **4c** *Directly from the Diene Complex* **9**: In a teflon coated autoclave a mixture of 20.0 g (0.15 mol) of anhydrous freshly powdered $AlCl_3$ and 3.75 g (15.0 mmol) of **9** in 100 ml of CS_2 was stirred for 3 h under 1 atm carbon monoxide. Then the carbon monoxide pressure was elevated to 120 atm and the solution was heated for 16 h at 120°C. After cooling the reaction mixture was hydrolyzed with ice and the mixture was extracted with three 100 ml portions of ether. The combined ether extractions were washed with water and dried over sodium sulfate. The solvents were evaporated in vacuo and the residue chromatographed on silica gel. With ether/hexane (1:1) first 480 mg (20%) of **4c** and then 270 mg (11%) of *1,4-dimethyl-8-hydroxybicyclo[3.2.1]oct-3-en-2-one* (**16**) were isolated upon recrystallization from ether/hexane (1:10) as colourless crystals, m.p. 70°C.

16: ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, 3H, 1-CH_3), 1.54 (m, 2H, CH_2), 1.86 (m, 1H, CH_2), 2.02 (d, J = <1 Hz, 3H, 4-CH_3), 2.38 (m, 1H, CH_2), 2.68 (s, 1H, OH), 2.69 (d, J = 6.5 Hz, 1H, 5-H), 3.69 (≈s, 1H, 8-H), 5.78 (d, J = 1 Hz, 1H, 3-H). – IR ($CHCl_3$): 3400 (br.), 1660 (m), 1630 (s) cm^{-1}. – MS (EI): *m/z* (rel. int.) = 166 (30%, M^+), 148 (4), 137 (26), 95 (100), 67 (25).

$C_{10}H_{14}O_2$ (166.2) Calcd. 166.09872 Found 166.0987

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