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Manganese(III)-mediated oxidative free-radical additions of 1,3-dicarbonyl compounds to homobenzonorbornadiene and benzobarrelene: mechanistic studies

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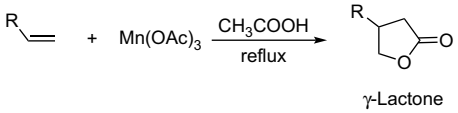
ABSTRACT

Homobenzonorbornadiene and benzobarrelene were reacted with dimedone/acetylacetone and $Mn(OAc)_3$ in the presence of $Cu(OAc)_2$ in acetic acid. Mainly rearranged products having a [2.2.2]skeleton and the nonrearranged dihydrofuran derivatives were obtained. These observations clearly indicated that the second oxidation takes place before the cyclization reaction. Furthermore, intramolecular tandem oxidations were observed where unusually oxyl radicals attack the double bond to form the products. The mechanism of the formation of the products is discussed.

1. Introduction

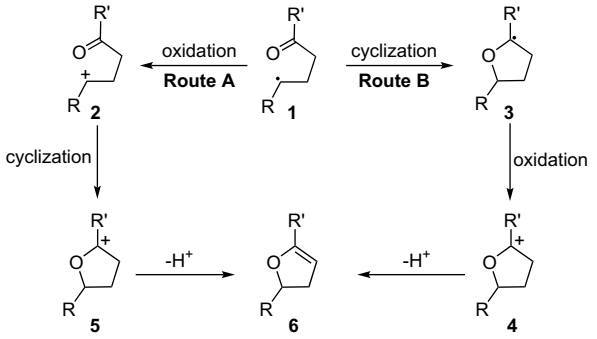
It has been known for a long time that manganese(III) acetate in acetic acid at reflux converts olefins to γ-lactons as shown below (Scheme 1).[1,2]



Scheme 1. Reaction of acetic acid with an alkene in the presence of $Mn(OAc)_3$.

On the other hand, the reaction of alkenes with 1,3-dicarbonyl compounds in the presence of $Mn(OAc)_3$ in acetic acid forms dihydrofurans.[3] The mechanism of this process has been viewed as generation of $^{\bullet}CH_2COR'$ followed by addition to the olefin, forming a new radical **1**. This radical can be reductively or oxidatively terminated.

Heiba and Dessau proposed oxidation of radical **1** to cation **2** followed by cyclization to the tetrahydrofuran derivative and then loss of a proton to give **6** (route A).[4] On the other hand, Fristad et al.[5] have proposed an alternative route B, where the formed radical **1** undergoes a cyclization reaction first, followed by oxidation (Scheme 2). We recently reacted benzonorbornadiene and heterobenzonorbornadienes with dimedone/acetylacetone and $Mn(OAc)_3$ in the presence and absence of $Cu(OAc)_2$.[6] We mainly obtained rearranged products. We concluded that the cyclization reaction takes place after the oxidation of the initially formed radical.



Scheme 2. General mechanism for the formation of dihydrofuran derivatives.

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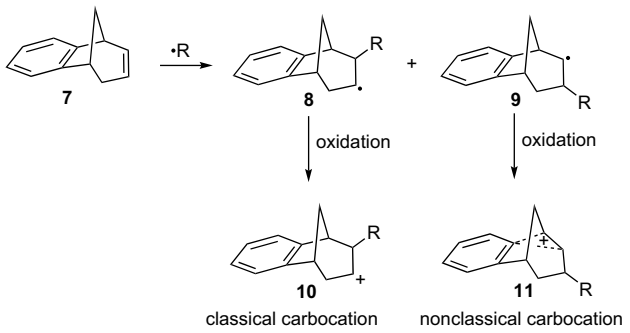
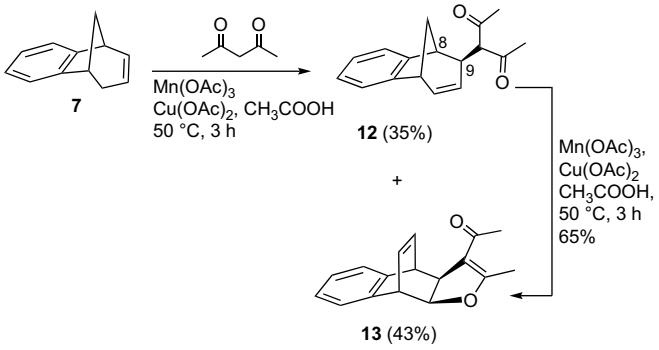


Scheme 3. Possible intermediates formed by addition of R˙ to homobenzonorbornadiene **7**.

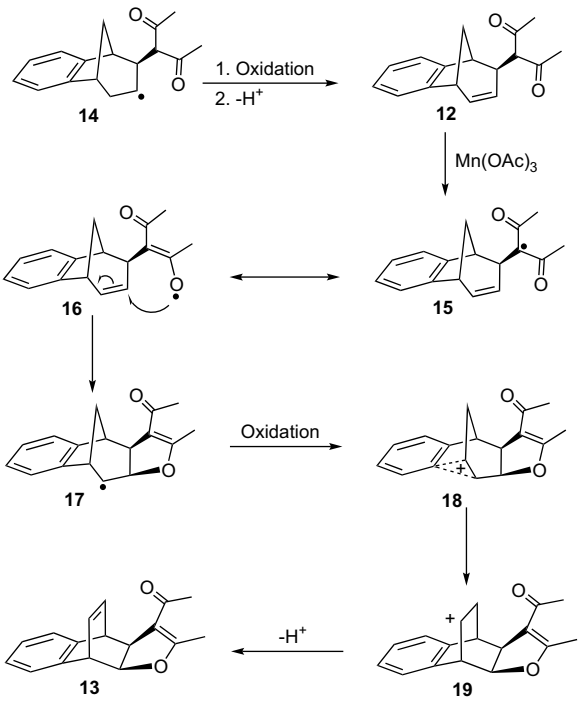
To gain more insight into the mechanism of cyclization reactions and the regioselectivity of the first addition we chose homobenzonorbornadiene **7**, which is capable of generating a classical carbocation as well a nonclassical carbocation **10** and **11**, respectively (Scheme 3). With these systems we might be able to study the regioselectivity of the addition as well as the behaviour of different carbocations on the mode of the reaction. Furthermore, a radical of type **9** does not undergo rapid rearrangement.[7] However, carbocation **11** has a great tendency for rearrangement to form rearranged products.[8] Therefore, the structure of the formed products derived from **10** as well as from **11** would give us information about the stage at which oxidation takes place.

2. Results and discussion

The starting material **7** was synthesized as described in the literature.[8b,9] We began our studies with the reaction shown in Scheme 4. The reaction of homobenzonorbornadiene **7** with



Scheme 4. Reaction of homobenzonorbornadiene **7** with acetylacetone and $Mn(OAc)_3$.



Scheme 5. Proposed mechanism for the formation of **12** and **13**.

$Mn(OAc)_3$ and acetylacetone in the presence of $Cu(OAc)_2$ in acetic acid at 50 °C gave two separable products: the nonrearranged product **12** and the rearranged product **13** in 35% and 43% yields, respectively (Scheme 4).

The structures of the formed products were unambiguously characterized by their NMR spectra (COSY, DEPT, HMBC and HMQC). The *exo*-configuration of the acetylacetone group in **12** was determined by measuring the coupling constant between H-8 and H-9 (J<2.0 Hz). Furthermore, the exact configuration of **13** was determined by X-ray crystallographic analysis (Fig. 1).

For the formation of those products we suggest the following mechanism (Scheme 5). The insertion product **12** can be formed by the addition of the initially formed radical derived from acetylacetone to the C=C double bond in **7** forming radical **14**, followed by oxidation of and loss of H^+. The fact that the rearranged product **13** contains an additional double bond can be rationalized by tandem oxidation of **7** with manganese(III) acetate. To test whether the rearranged product **13** is a primary or a secondary product, the nonrearranged product **12** was subjected to $Mn(OAc)_3$-oxidation

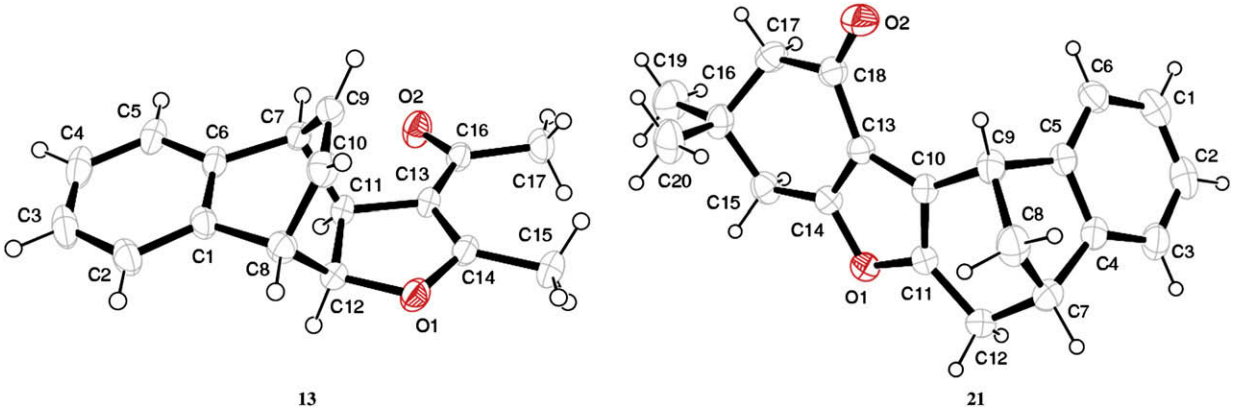
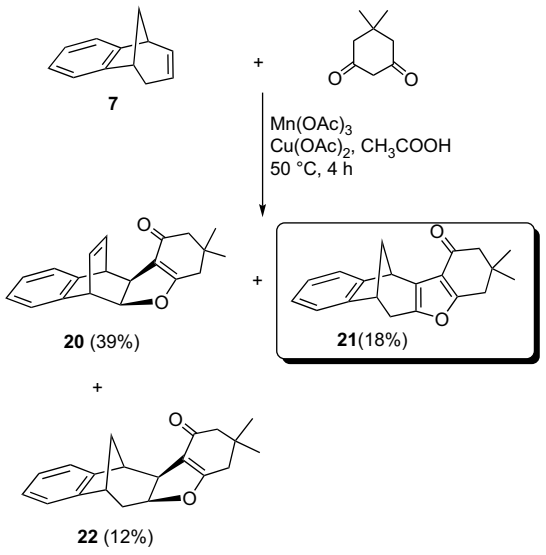


Figure 1. Thermal ellipsoid drawings of compounds **13** and **21**.

reaction under the same reaction conditions. The insertion product **12** was smoothly transferred by further oxidation into the rearranged product **13** in 65% yield. The reaction presumably proceeds via the formation of the tertiary radical **15**, which is in equilibrium with the oxyl radical **16**, and then this oxyl radical undergoes intramolecular addition to the double bond to afford a new secondary radical **17**. Rapid oxidation of this radical with $Cu(OAc)_2$ forms a nonclassical carbocation **18**, which is prone to Wagner–Meerwein rearrangement accompanying an aryl shift leading to the formation of a bicyclic[2.2.2]skeleton **19**. Deprotonation of the resulting carbocation can afford product **13**.

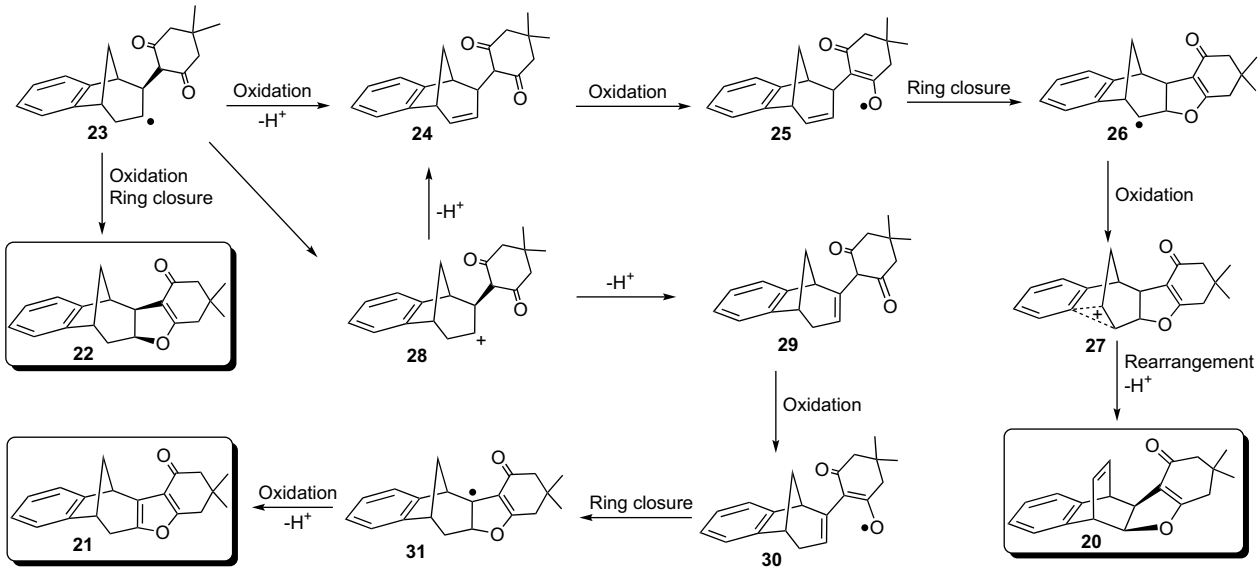
Tandem cyclizations are frequently encountered in the reactions initiated by Mn(III) acetate. There are four types of tandem cyclization reactions described in the literature.[1c,e] In the first three cases, the compounds have two different unsaturated fragments (double bond, triple bond or benzene ring).[10,3k,m,n] The forth tandem mode involves initial attack upon the double bond and then subsequent cyclization upon the alkoxycarbonyl or carboxy group.[11] In our case, the tandem cyclization is completely different from those described in the literature. The first step involves attack upon the double bond, followed by oxidative termination. In the second part of oxidation, the formed 1,3-dicarbonyl radical attacks intramolecularly a double bond with the oxygen atom not with the carbon atom. To the best of our knowledge, this is the first reported case where an oxyl radical attacks the carbon–carbon double bond. The termination of the newly formed radical may be oxidatively or reductively.



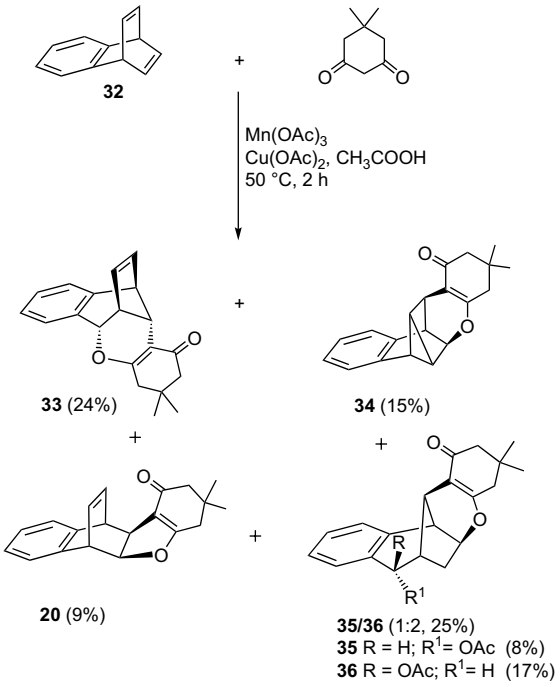
Scheme 6. Reaction of homobenzonorbornadiene **7** with dimedone and $Mn(OAc)_3$.

To gain more insight into the formation mechanism of **12** and **13**, dimedone was used instead of acetylacetone. The reaction of **7** with $Mn(OAc)_3$ and dimedone in the presence of $Cu(OAc)_2$ gave three separable products: the rearranged product **20** with [2.2.2]skeleton as the major product and two nonrearranged products **21** and **22** (Scheme 6). The structure of **20** was easily determined by 1D and 2D NMR spectra. The NMR spectral data of **22** were straightforward. The *exo*-configuration of the dihydrofuran ring in **22** was determined by measuring the coupling constant between the bridgehead hydrogen and the *tertiary* hydrogen atom. The exact structure of the furan derivative **21** was determined by X-ray analysis (Fig. 1). The striking difference in the product distribution of **7** by the reaction with dimedone may be attributed to the better enolizable ability of dimedone and the stability of the initially formed radical compared with the radical formed from acetylacetone.

The nonrearranged product **22** is an expected product. The formation of **22** can be rationalized by the addition of radical derived from dimedone to the double bond in **7** to give **23**, followed by oxidation with $Cu(OAc)_2$ to a classical cation, which can undergo rapid cyclization with the enol form of dimedone (Scheme 7). It is well established that the isolated primary and secondary radicals are not further oxidized by Mn(III), so that hydrogen abstraction from solvent or other reactions becomes the predominant reaction.[1] Heiba and Dessau found that $Cu(OAc)_2$ oxidizes secondary radicals 350 times faster than $Mn(OAc)_3$ does and two reagents can be used together.[4] Therefore, we assume that radical **23** undergoes oxidation before the cyclization. The formed classical carbocation **28**, may be stabilized by proton elimination to form Zatisev and Hofmann products **29** and **24**, respectively. The Zatisev product **29** can undergo further oxidation to form a new radical **30**. The intramolecular addition of oxyl radical **30** to the adjacent double bond can attack the double bond from the *exo*-face[12] and form the tertiary carbon radical **31**, which would further undergo oxidation



Scheme 7. Proposed mechanism for the formation of **20**–**22**.



Scheme 8. Reaction of benzobarrelene **32** with dimedone and $Mn(OAc)_3$.

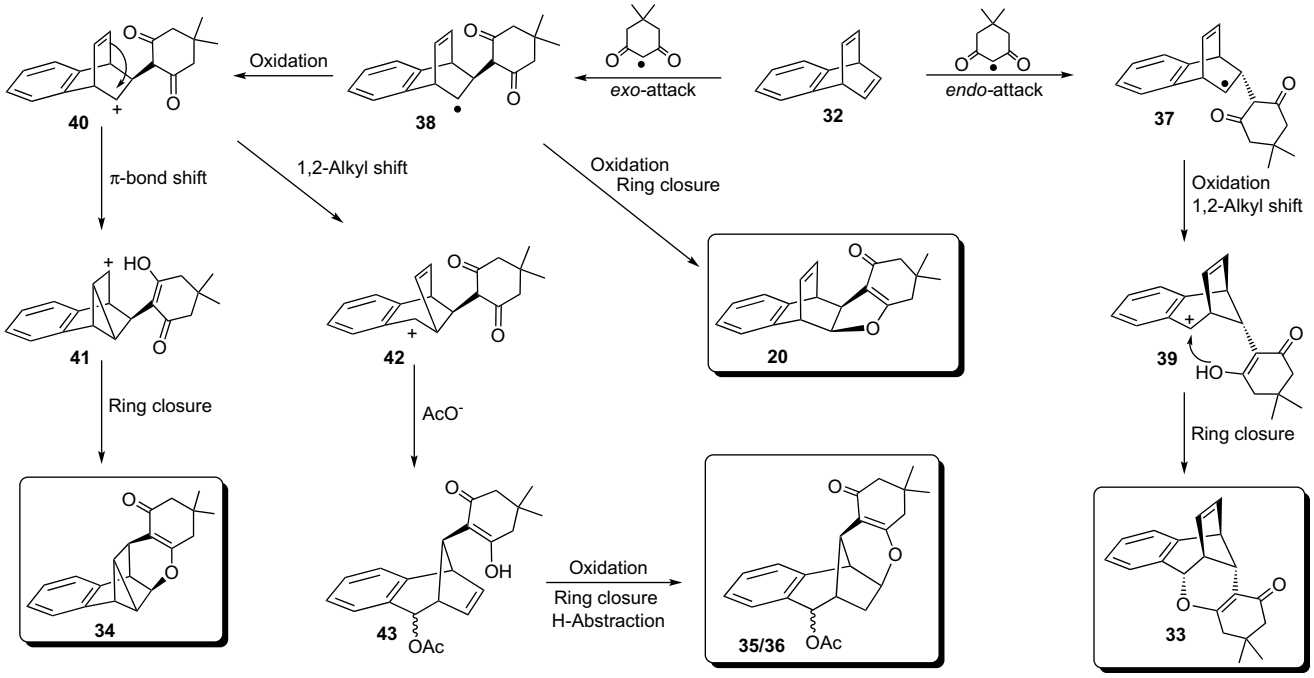
by Cu(II) acetate to form the corresponding carbocation. This cation would have a great tendency for Wagner–Meerwein rearrangement. However, the formation of an annelated dihydrofuran ring at the bridgehead would hinder the rearrangement. Therefore, the oxidation of **31** followed by H^+ loss will form the furan derivative **23**. To the best of our knowledge, this is the first reported case of the formation of a furan ring in $Mn(OAc)_3$ chemistry.

The formation of the major product **20**, can be rationalized as discussed by the formation of **13**. In this reaction, we were not able to detect the compound having structure **24**. Therefore, we assume that compound **25** is formed as an intermediate during this reaction. Since the 1,3-dicarbonyl unit in **24** can be oxidized more easily, than that in **12**, the formed intermediate **24** undergoes easily further oxidation reaction to form **25**, which can form **20** as depicted in Scheme 7.

In order to obtain further support for our proposed mechanism we reacted benzobarrelene **32** under the same reaction conditions with dimedone and acetylacetone. Treatment of **32** with dimedone in acetic acid and in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$ resulted in the formation of five different products **33**–**36** and **20**, along with the unreacted alkene, which was recovered in 4% yield (Scheme 8).

Column chromatography allowed us to isolate two separable rearranged products (**33**, **34**) and a nonrearranged dihydrofuran derivative **20**, besides a mixture containing two major rearranged isomers **35** and **36** in a ratio of 1:2, which were separated by fractional crystallization.

The structural determination of these products was carried out with 1D- and 2D-NMR (COSY, DEPT, HMQC and HMBC) spectral measurements. The formation mechanism of these products is outlined in Scheme 9. The radical generated from dimedone attacks the double bond in benzobarrelene from the *endo*- as well as the *exo*-face producing new radicals **37** and **38**, respectively. The oxidation of radical **37** provides an intermediate with a nonclassical carbocation character that undergoes an alkyl shift via Wagner–Meerwein rearrangement to form the rearranged benzylic cation **39**. A nucleophilic attack of the oxygen lone pair of the enol functionality on the cation leads to the formation of the major product **33**. For the mechanism of formation of the other products, we propose that the initially formed radical **38** first undergoes oxidation forming cation **40**, which is expected to rearrange accompanying alkyl or aryl migration.[13] Careful examination of the isolated fractions did not reveal any trace amounts of rearranged products resulting from the aryl migration process. This carbocation undergoes three competing reactions. The capture of the formed cation **40** by the hydroxyl oxygen of the enol form of dimedone will result in the formation of the nonrearranged product **20**. The cationic intermediate **40** can be attacked by the double bond electrons (double bond participation) forming a new carbocation **41**, which



Scheme 9. Proposed mechanism for the formation of **33**–**36** and **20**.

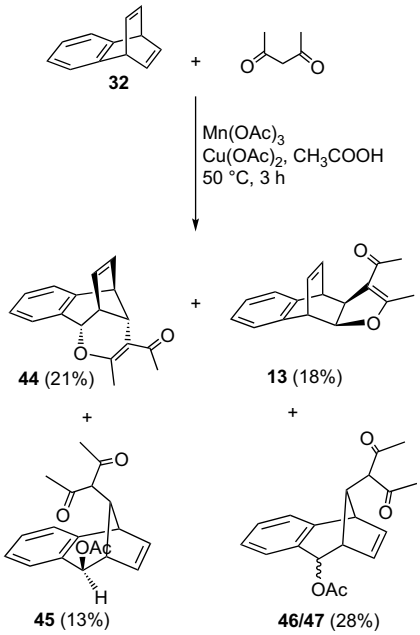
undergoes cyclization with the enol form of dimedone to give the cyclopropane compound **34**. Furthermore, the carbocation intermediate **40** can undergo an alkyl shift to form intermediate **42**, which is then captured by the acetate anion to give product **43** as a mixture of isomers. The rearranged intermediate **42** cannot undergo ring closure with the dimedone unit due to the *exo*-configuration of the dimedone unit in **42**. The rearranged intermediate **42** is then captured by the acetate anion to give product **43** as a mixture of isomers. The dimedone unit in **43** can now undergo further oxidation with Mn(III) acetate much faster than the starting material to furnish an electrophilic oxyl radical, which can add to the double bond in **43**. The formed radical will be then terminated reductively by abstraction of a hydrogen atom from the environment, producing the isomeric mixture **35**/**36** in 25% yield.

The oxidation of benzobarrelene **32** with acetylacetone in the presence of 2 equiv of $Mn(OAc)_3$ and 0.2 equiv of $Cu(OAc)_2$ in acetic acid for 3 h at 50 °C afforded besides the dihydrofuran derivative **13** two rearranged products **44** and **45**, and a mixture consisting of two isomers **46**/**47** (Scheme 10). The configuration of the acetoacetyl group in **45** and **46**/**47** was determined by measuring the coupling constants between the bridge and bridgehead protons.

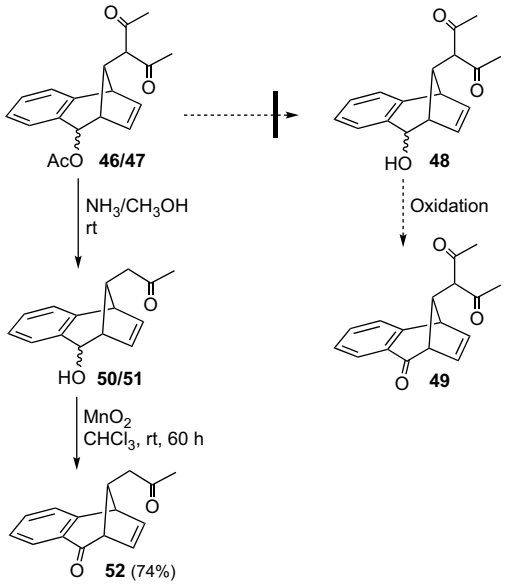
The isomeric mixture **46**/**47** could not be separated. We attempted to convert the isomeric mixture into a single isomer **49**. The acetate mixture was reacted with ammonia in methanol to remove the acetate groups. The obtained alcoholic mixture was subjected to a MnO_2 oxidation reaction without purification. Surprisingly, ammonia hydrolyzed acetates and removed one of the acetyl groups of acetylacetone moiety, as shown in Scheme 11.

The configuration of the acetyl functionality in **52** was assigned as *exo* on the basis of the lack of coupling between the bridge and bridgehead protons.

Analysis of the products obtained from the reaction of benzobarrelene **32** with acetylacetone (Scheme 10) indicates that the rearranged products are the major products and are formed in 62% yield, whereas the normal addition product, a nonrearranged product **13** was formed in 18% yield. We were not able to detect any compound having structures similar to those of **35** or **36** in spite of the fact that precursors **46**/**47** were formed. Further



Scheme 10. Reaction of benzobarrelene **32** with acetylacetone and $Mn(OAc)_3$.

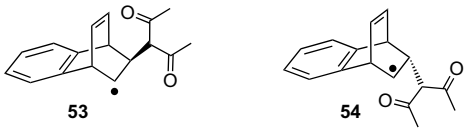


Scheme 11. Reaction of the mixture **46**/**47** with NH_3 followed by oxidation.

oxidation of **46** and **47** did not proceed probably due to the weak enolization of acetylacetone. For the formation of the rearranged products, we propose a mechanism similar to that as depicted in Scheme 9.

3. Conclusions

The primary goal of this work was to establish whether the second oxidation in the reaction of the $Mn(OAc)_3$ with bicyclic olefins (which have great tendency to undergo Wagner–Meerwein rearrangement) takes place before or after the cyclization.



Since we generally observe the rearranged products, we can conclude that free radicals **17**, **26**, **37**, **38**, **53** and **54** are oxidized before cyclization occur, and then nonclassical carbocations are produced, which induce Wagner–Meerwein rearrangement in the bicyclic system, leading to the formation of the rearranged products. An unexpected observation in this work was the formation of a unique tandem oxidation product, furan derivative **21**. Furthermore, the unusual electrophilic oxyl-radicals **16**, **25** and **30** and the radical derived from **43** (which has not been reported in $Mn(OAc)_3$-based oxidative cyclization) were the attacking species in the reaction of the formation of rearranged products **13**, **20**, **21** and **35**/**36**, respectively.

In the case of the [2.2.2]system, benzobarrelen **32**, 1,3-dicarbonyl free-radical additions took place from the *endo*- as well as the *exo*-face of the double bond and led mainly to alkyl- and π-bond shift products, while the aryl shift product was not formed.

4. Experimental

4.1. General

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 Series FT-IR spectrometer. The ^1H and ^{13}C NMR spectra were recorded on 400 (100) and 200 (50) MHz spectrometers. Apparent splitting is given in all cases. Column

chromatography was performed on silica gel (60-mesh, Merck) and TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminium-backed plates. All substances reported in this paper are in their racemic form. MnO_2 used in the oxidation reaction was prepared from potassium permanganate and manganese sulfate as described in the literature.[14]

4.2. General procedure for $Mn(OAc)_3$ reaction

A solution of 1,3-diketone (5 mmol) and olefin (5 mmol) in glacial acetic acid (20 mL) in a flame-dried flask was heated to 50 °C under nitrogen. A 10 mmol portion of $Mn(OAc)_3 \cdot 2H_2O$ and 2 mmol of $Cu(OAc)_2$ were then added to the solution. The dark brown solution became lighter as the Mn(III) was reduced. When the reaction was complete, the solution was colourless to light blue-green with variable amount of white precipitate present. Water was added to the reaction mixture, and the precipitate was dissolved. The solution was extracted with methylene chloride. The combined organic layers were washed several times with saturated $NaHCO_3$ solution and the water and dried ($MgSO_4$). Evaporation of the solvent gave the crude compound, which was purified by crystallization or column chromatography.

4.3. Oxidative addition of acetylacetone to 7 in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$

Acetylacetone (0.5 g, 5 mmol), homobenzonorbornadiene (**7**) (0.78 g, 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.18 g, 1 mmol) in 25 mL of glacial acetic acid were reacted for 3 h as described above. The chromatography of the residue (1.13 g) on silica gel (4:1 hexane/EtOAc) gave 0.445 g of **12** (35%) and 0.55 g of **13** (43%).

*4.3.1. 1S,2R,9R,-(rel)Tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,10-tetraen-9-ylpentane-2,4-dione (**12**)*

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J=7.2 Hz, 1H, arom), 7.14–7.06 (m, 3H, arom), 6.26 (dd, J=8.1 and 6.0 Hz, H-11), 4.96 (dt, J=8.1 and 1.7 Hz, H-10), 3.88 (d, J=11.0 Hz, H-3′), 3.31 (dd, J=6.0 and 4.6 Hz, H-1), 3.01 (br d, J=11.0 Hz, H-9), 2.89 (br d, J=4.6 Hz, H-8), 2.30 (s, 3H), 2.22 (dt, J=10.4 and 4.6 Hz, H-12$_{exo}$), 2.19 (s, 3H), 2.00 (d, J=10.4 Hz, H-12$_{endo}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 202.3, 151.2, 144.9, 137.0 (C-11), 126.3 (2C), 123.7, 123.2 (C-10), 120.6, 72.2 (C-3′), 42.8 (C-8), 41.2 (C-9), 40.9 (C-1), 37.1 (C-12), 29.5 (-CH_3), 29.1 (–CH_3); IR (KBr, cm^{-1}): 3431, 3286, 3051, 2961, 2924, 1633, 1461, 1402, 1215, 1140, 1047. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.60; H, 6.88.

*4.3.2. 1R,8S,9R,13R-(rel)-1-(11-Methyl-10-oxatetracyclo-[6.5.2.0^{2,7}.0^{9,13}]pentadeca-2,4,6,11,14-pentaen-12-yl)-ethan-1-one (**13**)*

Pale yellow needless, mp 143–145 °C; H NMR (400 MHz, $CDCl_3$) δ 7.0–7.20 (m, 4H, arom), 6.43 (quasi t, J=6.8 Hz, 1H), 6.34 (quasi t, J=6.8 Hz, 1H), 4.74 (dd, J=9.3 and 8.3 Hz, 1H, H_{9a}), 4.31–4.39 (m, 2H), 3.36 (br d, J=3.9 Hz, 1H), 2.12 (s, 3H, –CH_3), 2.25 (s, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 169.8, 143.7, 138.8, 135.2, 130.7, 126.3, 125.5, 124.3, 123.6, 115.7, 84.8, 51.0, 45.2, 43.0, 29.1, 15.4; IR (KBr, cm^{-1}) 3059, 2974, 2926, 1627, 1610, 1386, 1220, 1147, 989. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.75; H, 6.48.

*4.3.3. Transformation of **12** to **13***

Diketone **12** (0.5 g, 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (1.35 g, 5 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.09 g, 0.5 mmol) in 20 mL of glacial acid acetic acid were reacted for 3 h as described above. The chromatography of the residue on a short silica gel (4:1 hexane/EtOAc) afforded 0.32 g of **13** (65%).

4.4. Oxidative addition of dimedone to homobenzonorbornadiene (7) in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$

Dimedone (0.7 g, 5 mmol), homobenzonorbornadiene (0.78 g, 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.18 g, 1 mmol) in 20 mL of glacial acetic acid were reacted for 4 h as described above. The chromatography of the residue on silica gel (160 g, 4:1 hexane/EtOAc) afforded the unreacted alkene **7** as a first fraction (0.18 g, 23%), followed by product **21** (201 mg, 18%), **22** (0.146 g, 12%) and the rearranged product **20** (0.44 g, 39%) (the yields are based on the consumed starting material).

*4.4.1. 1R,12S-(rel)-4-Oxa-7,7-dimethylpentacyclo-[10.6.1.0^{3,11}.0^{5,10}.0^{13,18}]nona-deca-5(10)-3(11),13,15,17-pentaen-9-one (**21**)*

Colourless needles, mp 129–131 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.17 (m, 1H, arom), 7.12 (dd, J=7.1 and 1.7 Hz, 1H, arom), 6.99–6.93 (m, 2H, arom), 4.27 (d, $J_{12,19exo}$=4.2 Hz, H-12), 3.52 (dd, $J_{1,2exo}$=5.0 Hz and $J_{1,19exo}$=4.6 Hz, H-1), 3.04 (dd, A-part of AB-system, $J_{2endo,2exo}$=16.3 Hz and $J_{1,2endo}$=5.0 Hz, H-2$_{endo}$), 2.52 (s, 2H), 2.49 (d, B-part of AB-system, J=16.3 Hz, H-2$_{endo}$), 2.35 (dt, A-part of AB-system, $J_{19endo,19exo}$=10.4 Hz and $J_{19exo,1}$=$J_{19exo,12}$=4.6 Hz, H-19$_{exo}$), 2.22 (s, 2H), 1.96 (d, B-part of AB-system, $J_{19endo,19exo}$= 10.4 Hz, H-19$_{endo}$), 1.05 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 163.8, 151.9, 147.0, 144.2, 126.7, 126.1, 123.6, 123.0, 121.2, 117.5, 52.4, 42.4, 40.0, 37.7 (2C), 35.1, 30.8, 29.1, 28.5; IR (KBr, cm^{-1}): 3020, 2963, 2941, 1668, 1565, 1461, 1348, 1280, 1230. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.36; H, 7.07.

*4.4.2. 5aS,7S,12S,12aS-(rel)-3,3-Dimethyl-2,3,4,5a,6,7,12,12a-octahydro-1H-7,12-methanobenzo[b]benzo[5,6]cyclohepta-[1,2-d]furan-1-one (**22**)*

Colourless crystals, mp: 133–134 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.36–7.31 (m, 1H, arom), 7.10–6.95 (m, 3H, arom), 4.40 (dt, J=8.4 and 6.7 Hz, H-3), 3.72 (br s, 1H), 3.29 (d, J=8.9 Hz, 1H), 3.03 (br s, 1H), 2.28–2.06 (m, 6H), 1.75 (m, 1H), 1.71 (d, J=11.9 Hz, 1H), 1.11 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 172.0, 142.6, 141.8, 122.7, 122.6, 118.7, 118.3, 109.5, 78.3, 47.2, 40.6, 36.8, 34.0, 34.0, 33.2, 32.0, 29.9, 24.46 (2C); IR (KBr, cm^{-1}) 3019, 2957, 2868, 1721, 1621, 1467, 1400, 1278, 122.9. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 82.02; H, 7.40.

*4.4.3. 1S,2R,10R,11R,12S-(rel)-3-Oxa-6,6-dimethylpentacyclo-[9.6.2.0^{2,10}.0^{4,9}.0^{12,17}]nona-deca-4(9),12,14,16-tetraen-8-one (**20**)*

Colourless crystals, mp 132–133 °C from EtOAc/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (br d, J=6.7 Hz, 1H, arom), 7.20 (br d, J=7.1 Hz, 1H), 7.13–7.05 (m, 2H, arom), 6.46 (dd, J=7.6 and 6.7 Hz, H-18), 6.38 (br t, J=6.7 Hz), 4.94 (dd, J=8.9 and 2.7 Hz, H-2), 4.46 (dd, J=6.7 and 1.5 Hz, H-1), 4.36 (br t, J=6.5 Hz, H-19), 3.35 (br d, J=8.9 Hz, H-10), 2.23 (dd, A-part of AB-system, J=17.4 and 1.6 Hz, 1H), 2.20 (d, A-part of AB-system, J=16.1 Hz, 1H), 2.16 (d, B-part of AB-system, J=17.4 Hz, 1H), 2.13 (d, B-part of AB-system, J=16.1 Hz, 1H), 1.12 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (C-8), 178.1 (C-4), 143.8 (C1-7), 138.4 (C-12), 135.8 (C-18), 130.4 (C-19), 126.5, 125.6, 124.4, 123.8, 113.6 (C-9), 88.2 (C-2), 51.0 (C-5 or C-7), 47.0 (C-10), 45.1 (C-11), 42.2 (C-1), 37.8 (C-5 or C-7), 34.1 (C-6), 29.6 (–CH_3), 27.9 (–CH_3); IR (KBr, cm^{-1}) 3051, 2961, 2924, 1633 (C=O), 1461, 1402, 1365, 1215, 1140, 1047. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.09; H, 6.90. Found: C, 82.23; H, 7.09.

4.5. Oxidative addition of dimedone to benzobarrelene (32) in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$

Dimedone (0.7 g, 5 mmol), benzobarrelene (**32**) (0.77 g, 5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (2.7 g, 10 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.18 g, 1 mmol) in 20 mL of glacial acetic acid were reacted for 2 h

as described above. The chromatography of the residue (1.35 g) on silica gel (150 g, 4:1 hexane/EtOAc) afforded the unreacted alkene as a first fraction (32 mg, 4%), followed by **33** (350 mg, 24%), **34** (219 mg, 15%), **20** (130 mg, 9%) and then a fifth fraction which consisted of a mixture of **34**/**35** in a ratio of 1:2 with a total yield (440 mg, 25%), this mixture was subjected to fractional crystallization. Firstly, the *endo*-derivative **35** was crystallized from hexane–AcOEt (4:1) in refrigerator during 1 day (0.12 g, 6.5%). After filtration of **35** the solvent was evaporated and the oily residue was crystallized from hexane–AcOEt (3:1) to give **36**. Repeated crystallization gave the analytically pure samples.

*4.5.1. 6S,11S,12S,13R-(rel)-3,3-Dimethyl-2,3,4,6,11,12-hexahydro-1H-11,6,12-prop[1]ene[1,3,3]triyldibenzo-[b,f]oxocin-1-one (**33**)*

Colourless solid, mp 135–138 °C from hexane–AcOEt (3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.04 (m, 2H, arom), 6.98 (dt, J=7.3 and 2.8 Hz, 1H, arom), 6.82 (d, J=7.3 Hz, 1H, arom), 6.58 (dd, J=5.7 and 3.1 Hz, H-15), 5.84 (dd, J=5.7 and 3.0 Hz, H-14), 5.07 (br d, J=2.7 Hz, H-6), 3.53 (dd, J=4.5 and 3.1 Hz, H-11), 3.25 (br t, J=4.5 Hz, H-12), 2.71–2.68 (m, H-13), 2.16 (d, A-part of AB-system, J=17.0 Hz, 1H, H-4), 2.04 (d, A-part of AB-system, J=16.2 Hz, 1H, H-2), 1.97 (d, B-part of AB-system, J=16.2 Hz, 1H, H-2′), 1.86 (d, B-part of AB-system J=17.0 Hz, 1H, H-4′), 0.94 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 (C-1), 168.7 (C-4a), 147.4 (C-15), 143.6 (C-10a), 131.6 (C-6a), 131.0 (arom), 128.8 (C-14), 128.0 (arom), 127.1 (arom), 125.5 (arom), 113.9 (C-12a), 74.1 (C-6), 50.4 (C-2), 49.9 (C-11), 42.1 (C-4), 41.9 (C-12), 41.1 (C-13), 32.2 (C-3), 28.1 (CH_3), 28.0 (CH_3); IR (KBr, cm^{-1}): 3281, 3057, 2957, 2953, 2924, 2866, 1652, 1621, 1456, 1386, 1342, 1244, 1207, 1170. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89; O, 11.05. Found: C, 82.51; H, 7.15.

*4.5.2. 4bS,5R,10bR,11S,12S,13S-(rel)-8,8-Dimethyl-4b,5,7,8,9,10b,11,12-octahydro-10H-5-11,12-methanetriylnaphtho[1,2-c]-chromen-10-one (**34**)*

White solid, mp 143–145 °C from EtOAc/*n*-hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J=7.0 Hz, 1H, arom), 7.17 (br t, J=7.4 Hz, 1H, arom), 7.13 (dt, J=7.2 and 1.2 Hz, 1H, arom), 4.35 (s, H-5), 3.04 (br s, H-10b), 2.73 (br s, H-4b), 2.25 (AB-system, J=16.1 Hz, –CH_2–), 2.24 (AB-system, J=17.3 Hz), 2.08 (t, J=7.2 Hz, H-12), 2.01 (br t, J=7.2 Hz, H-13), 1.78 (br t, J=7.2 Hz, H-11), 1.11 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 168.7, 134.4, 134.2, 127.1, 125.4, 125.2, 125.16, 116.5, 82.1, 50.4, 41.9, 41.7, 32.5, 29.7, 28.6, 28.2, 25.7, 20.9, 17.9; IR (KBr, cm^{-1}) 3069, 3028, 2951, 2916, 2849, 1646, 1614, 1490, 1465, 1380, 1303, 1202, 1120, 1037, 980, 760, 721, 506. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.89; O, 11.05. Found: C, 82.16; H, 6.87.

*4.5.3. 4R,5R,10bR,11S,12R-(rel)-8,8-Dimetyl-10-oxo-4b,7,8,9,10,10b,11,12-octahydro-5H-5,11-methanonaphtho[1,2-c]-chromen-12-yl acetate (**35**)*

White solid, mp: 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–7.20 (m, 4H, arom), 6.16 (d, J=4.3 Hz, H-12), 4.61 (d, J=5.4 Hz, H-5), 3.27 (br s, H-10b), 2.91 (br s, H-4b), 2.87 (br t, J=4.3 Hz, H-11), 2.21–2.11 (AB-system, J=16. 3 Hz, –CH_2–), 2.19 (dd, J=16.7 and 5.4 Hz, H-13$_{exo}$), 2.15 (s, –CH_2–), 2.04 (s, 3H), 1.8 (dd, J=16.7 and 5.9 Hz, H-13$_{endo}$), 1.01 (s, 3H), 9.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 169.6, 167.0, 136.8, 132.8, 127.2, 127.1, 126.9, 126.8, 115.2, 83.2, 72.7, 49.4, 46.3, 44.1, 40.6, 35.7, 31.5, 30.5, 27.8, 26.9, 20.2; IR (KBr, cm^{-1}): 3067, 3032, 2963, 2886, 2864, 1729, 1648, 1623, 1390, 1253, 1234, 1051, 1030, 989, 929, 754, 606, 559. Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.07; H, 7.05.

*4.5.4. 4R,5R,10bR,11S,12S-(rel)-8,8-Dimetyl-10-oxo-4b,7,8,9,10,10b,11,12-octahydro-5H-5,11-methanonaphtho[1,2-c]chromen-12-yl acetate (**36**)*

Colourless powder, mp: 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 3H, arom), 7.22–7.19 (m, 1H, arom), 5.59 (d, J=3.2 Hz, H-12), 4.60 (d, J=5.4 Hz, H-5), 3.45 (br s, H-10b), 3.10 (br s, H-4b), 2.83 (br d, J=7.5 Hz, H-11), 2.28–2.19 (AB-system, J=16.2 Hz, 2H, H-9 or H-7), 2.22 (s, 2H, H-7 or H-9), 2.13 (s, 3H), 2.07 (dd, J=15.7 and 8.2 Hz, H-13$_{exo}$), 1.64 (dd, J=15.7 and 5.4 Hz, H-13$_{endo}$), 1.08 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6 (C-10), 170.8 (CO–CH_3), 167.8 (C-6a), 138.6 (C-4A), 132.1 (C-12a), 130.9, 128.8, 128.4, 127.9, 116.1, 83.1 (C-5), 73.3 (C-12), 50.5 (C-7 or C-9), 47.2 (C-11), 44.8 (C-4b), 41.4 (C-7 or C-9), 33.4 (C-13), 32.5 (C-10b), 31.9 (C-8), 28.7 (CH_3), 28.0 (CH_3), 21.4 ($COCH_3$); IR (KBr, cm^{-1}): 3022, 2953, 2936, 2886, 1725, 1646, 1616, 1390, 1238, 1122, 1020. Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.32; H, 6.99.

4.6. Oxidative addition of acetylacetone to benzobarrelene (32) in the presence of $Mn(OAc)_3$ and $Cu(OAc)_2$

Acetylacetone (0.5 g, 5 mmol), benzonorbornadiene (**32**) (0.78 g, 5 mmol), $Mn(OAc)_3\cdot 2H_2O$ (2.7 g, 10 mmol) and $Cu(OAc)_2\cdot 2H_2O$ (0.18 g, 1 mmol) in 25 mL of glacial acetic acid were reacted for 3 h as described above. The chromatography of the residue (1.25 g) on silica gel (4:1 hexane/EtOAc) gave **44** (268 mg, 21%) as the first fraction followed by **13** (230 mg, 18%), **45** (205 mg, 13%) and a mixture consisting of **46**/**47** (443 mg, 28%).

*4.6.1. 1S,5R,6R,12S-(rel)-1-(3-Methyl-5,6-dihydro-1H-6,1,5-prop[1]ene[1,3,3]triyl-2-benzoxocin-4-yl)ethanone (**44**)*

Colourless crystals, mp 118–120 °C from hexane–AcOEt (3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–7.18 (m, 3H, arom), 6.90 (br d, J=7.2 Hz, 1H, arom), 6.63 (dd, J=5.6 and 3.1 Hz, H-12), 5.96 (dd, J=5.6 and 3.2 Hz, H_{11}), 5.09 (d, J=3.0 Hz, H-1), 3.53 (t, J=3.2 Hz, H-6), 3.34 (t, J=4.2 Hz, H-5), 2.76 (dt, J=4.2 and 3.1 Hz, H-13), 2.27 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 164.1, 146.3, 142.7, 131.3, 131.1, 129.1, 128.0, 127.4, 125.2, 114.1, 72.7, 50.9, 46.2, 41.0, 29.6, 20.6. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.58; H, 6.54.

*4.6.2. 10-(1-Acetyl-2-oxopropyl)-8,9-dihydro-5H-5,8-methanobenzo[a][7] annulen-9-yl (**45**)*

White needles, mp 95–97 °C from EtOAc/*n*-hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dt J=7.6 and 1.0 Hz, 1H, arom), 7.22–7.17 (m, 2H, arom), 6.95 (br d, J=7.0 Hz, 1H, arom), 6.53 (dd, J=5.7 and 3.2 Hz, H-7), 6.06 (dd, J=5.7 and 3.3 Hz, H-6), 5.68 (br s, 1H, H-9), 3.97 (d, A-part of AB-system, J=12.0 Hz, H-11), 3.23 (dt, J=12.0–4.0 Hz, H-10), 3.17 (t, J=3.4 Hz, H-5), 2.94 (br s, 1H, H-8), 2.16 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 201.2, 170.0, 144.4, 139.4, 133.1, 130.7, 130.6, 128.0, 127.8, 126.5, 68.4, 67.6, 46.5, 46.0, 44.4, 30.0, 28.7, 21.1; IR (KBr, cm^{-1}): 3061, 2995, 2970, 2938, 1737, 1698, 1419, 1359, 1290, 1224, 1145, 960. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.84; H, 6.67.

4.7. 10-(2-Oxopropyl)-5,8-dihydro-9*H*-5,8-methanobenzo[*a*][7]annulen-9-one (52)

The isomeric acetate mixture **46**/**47** (100 mg, 0.32 mmol) was dissolved in 50 mL of abs methanol. As dry NH_3 passed through the solution, the mixture was stirred for 4 h at room temperature. Evaporation of the solvent gave 80 mg of crude product (**50**/**51**), which was dissolved in 50 mL of chloroform and freshly prepared MnO_2 (1.0 g, 11.5 mmol) was added. The solution was stirred at room temperature for 60 h. After filtration and evaporation of the solvent, the residue was crystallized from hexane/EtOAc (3:1) to give **52** (54 mg, 74%). White crystals, mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (br d, J=7.4 Hz, H-1), 7.34 (dt, J=7.3 and 1.5 Hz, 1-H, arom), 7.28 (dt, J=7.3 and 1.4 Hz, 1-H, arom), 7.12 (dd, J=7.3 and 1.3 Hz, H-4), 6.56 (dd, J=5.2 and 3.0 Hz, H-7), 5.98 (dd, J=5.2 and 3.3 Hz, H-6), 3.49 (br d, J=3.0 Hz, H-8), 3.31 (dd, J=8.1 and 5.9 Hz, H-10), 3.25 (d, J=3.3 Hz, H-5), 2.74 (dd, A-part of AB-system,

J=17.3 and 8.1 Hz, H-11), 2.62 (dd, B-part of AB-system, J=17.3 and 5.9 Hz, H-11′), 2.15 (s, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 195.6, 148.5, 143.9, 133.5, 130.0, 129.6, 129.3, 128.3, 125.7, 61.3, 54.8, 52.2, 45.5, 50.5; IR (KBr, cm^{-1}): 3031, 2985, 1737, 1698, 1224, 1145, 960. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.86; H, 6.35.

CCDC 681161 (for compound **13**) and CCDC 681140 (for compound **21**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

^1H and ^{13}C NMR spectra for all new compounds and crystallographic information files (CIFs) for compounds **13** and **21** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.012.

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