Manganese(III) Acetate Catalyzed Oxidative Radical Additions of α-Dicarbonyl Compounds to 1- and 2-Phenylcyclohepta-1,3,5-triene

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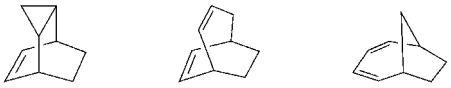
Manganese(III) acetate catalyzed oxidative radical-addition reactions of α-dicarbonyl compounds such as methyl acetoacetate (**6**), acetylacetone (**7**), and dimedone (**8**) to the mixture of 1- and 2-phenylcyclohepta-1,3,5-triene (**4** and **5**) were investigated (*Scheme 1*). The 1-phenylcyclohepta-1,3,5-triene (**4**) formed mainly [2+3] and [4+3] dihydrofuran addition products derived from cycloheptatriene and [2+3] dihydrofuran addition products derived from the norcaradiene structure. The 2-phenylcyclohepta-1,3,5-triene (**5**) formed mainly [6+3] dihydrofuran addition products derived from cycloheptatriene and [4+3] dihydrofuran addition products derived from the norcaradiene structure. The structures of isolated products were established by their spectroscopic data (IR, ^{1}H- and ^{13}C-NMR, MS, and elemental analysis) and comparison with literature data. The formation mechanism of the products is discussed.

Introduction. – $Mn(OAc)_3$-Promoted additions of 1,3-dicarbonyl compounds to alkenes [1], sterically hindered alkenes [2], bicyclic alkenes [3], alkynes [4], imines [5], α,β-unsaturated amides [6], and α,β-unsaturated ketones [7] such as chalcones have been reported. But, there are only a few studies on the addition of 1,3-dicarbonyl compounds to conjugated diene and triene systems particularly cycloheptatriene (CHT) [8]. Moreover, CHT is known to undergo the *Diels–Alder* reaction with various dienophiles [9]. In most cases, the formed adduct possesses a tricyclo[3.2.2.0^{2,4}]nonane skeleton **1** instead of that of a simple [2+4] cycloadduct **2**. The skeleton of type **3** is formed by [2+6] cycloaddition reactions [9].



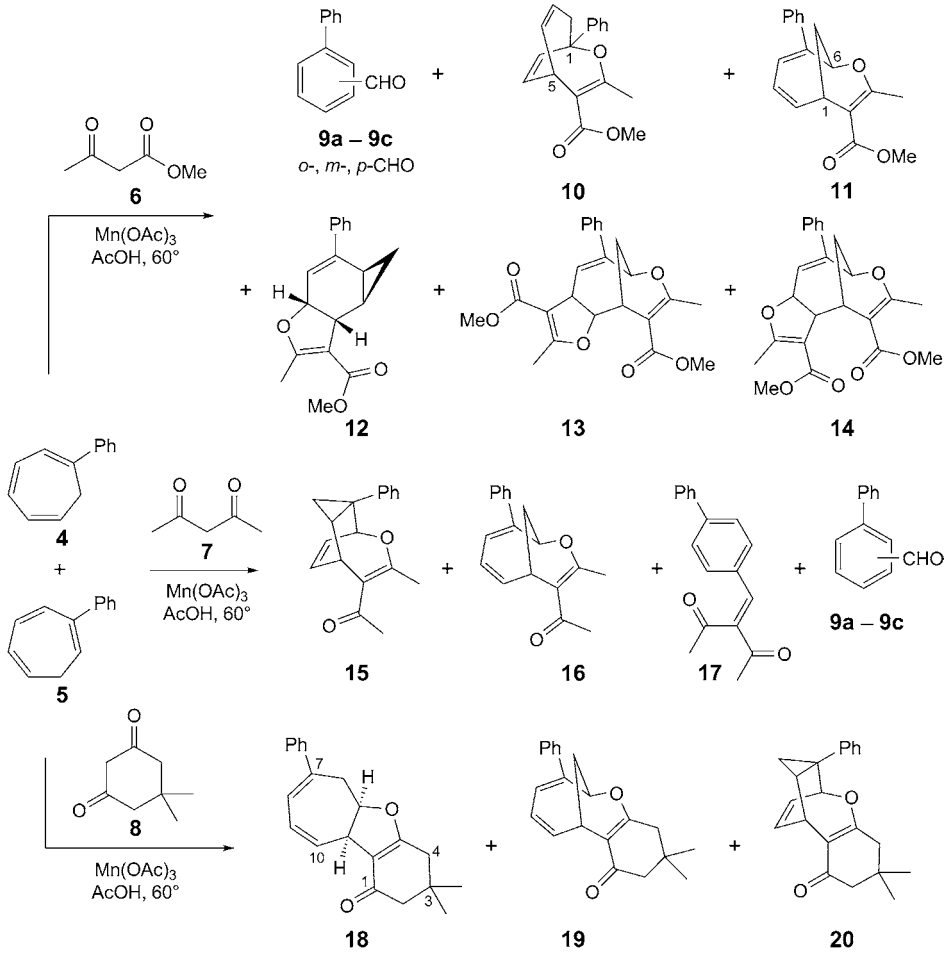
1 **2** **3**

In this work, we investigated the reactions of 1- and 2-phenylcyclohepta-1,3,5-triene (**4** and **5**) with 1,3-dicarbonyl compounds and found cycloadducts of types **2** and **3** besides products of type **1**.

Results and Discussion. – The starting materials **4** and **5** were synthesized as described in our recently published report [10]. The reaction of the mixture **4**/**5** with $Mn(OAc)_3$ and methyl acetoacetate (= methyl 3-oxobutanoate; **6**) in AcOH at 60°

gave eight products: three rearrangement products **9a**–**9c**, three 1:1 adducts, namely the $[4+3]\pi$ adduct **10**, the $[6+3]\pi$ adduct **11**, and the $[2+3]\pi$ adduct **12** (*via* the norcaradiene structure of **5**), and two 1:2 adducts **13** and **14** (*Scheme 1*). The products **9**–**14** were isolated by repeated silica-gel column chromatography.

Scheme 1



The structures of the [1,1′-biphenyl]carboxaldehydes **9a**–**9c** were determined by spectroscopic data and comparison with authentic samples [10]. In the addition reaction of 1,3-dicarbonyl compounds to cycloheptatriene derivatves, similar rearrangements have been reported by *Tsuruta et al.* [8] from the reaction of cycloheptatriene-7-carboxaldehyde and of its dimethyl acetal. Moreover, the rearrangement products [1,1′-biphenyl]carboxaldehydes **9a**–**9c** have been obtained by oxidation of **4** and **5** with air O_2 and/or CrO_3 [10].

The $[4+3]\pi$ adduct **10** of **4** exhibited the signals of four olefinic H-atoms and nine aliphatic H-atoms in the ^{1}H-NMR spectrum and only one signal for a C=O group in the

^{13}C-NMR spectrum. The molecular-ion peak in the MS at *m/z* 282 (M^+) indicated a 1:1 adduct. The CH_2 group resonated as an *AB* part of an *ABXY* system (two *ddd*) at δ(H) 2.47 and 2.32 with coupling constants $J = 20.0$, 9.6, and 2.0 Hz. The ^2J coupling of the CH_2 moiety ($J = 20.0$ Hz) is in agreement with literature data. *Asao* and co-workers [11] have obtained a type-**2** cycloadduct from the reaction of CHT and singlet oxygen; and they reported a ^2J value of 19.0 Hz. Consequently, **10** must be the $[4+3]\pi$ cycloadduct of **4**.

The $[6+3]\pi$ adduct **11** of **5** showed the signals of three olefinic H-atoms and ten aliphatic H-atoms in the ^{1}H-NMR spectrum and again one signal for a C=O group in the ^{13}C-NMR spectrum. The molecular-ion peak at *m/z* 282 (M^+) indicated a 1:1 adduct. The three olefinic H-atoms resonated at δ(H) 6.26–6.21 as a *m*. While the bridgehead H–C(6) gave rise to a *d* at δ(H) 5.15 ($J = 9.2$ Hz), its counterpart H–C(1) resonated as a *t* at δ(H) 3.43 ($J = 10.2$ Hz). The H-atoms of the CH_2 bridge appeared as a *d* at δ(H) 2.91 ($J = 12.8$ Hz) and a *dd* at δ(H) 2.52 ($J = 12.8$, 10.2 Hz). A similar structure and spectral results were obtained by *Mori* and *Takeshita* [12] for the addition product of 1,4-benzoquinone to cycloheptatriene.

The $[2+3]\pi$ adduct **12** of methyl acetoacetate (**6**) and the norcaradiene (= bicyclo[4.1.0]heptadiene) valence isomer of **5** showed the olefinic H-atom as *d* at δ(H) 5.74 ($J = 4.0$ Hz) and the neighboring H-atom as *dd* at δ(H) 4.97 ($J = 10.8$ and 4.0 Hz). The coupling constant ($J = 4.0$ Hz) clearly indicated a vicinal position of the two H-atoms. Moreover, the signal at δ(H) 0.22 established the presence of a cyclopropane ring in the structure. Moreover, the molecular-ion peak at *m/z* 282 (M^+) was in accordance with the structure.

The adducts **13** and **14** turned out to be formed from **6** and **11**. Their NMR spectrum showed that they were isomers of each other. Furthermore, the signal of one olefinic H-atom in the ^{1}H-NMR spectrum and two signals for 2 C=O groups in the ^{13}C-NMR spectrum as well as the molecular-ion peak at *m/z* 396 (M^+) in the MS clearly indicated the presence of two methyl acetoacetate units.

The reaction of the mixture **4/5** with $Mn(OAc)_3$ and acetylacetone (= pentane-2,4-dione; **7**) in AcOH at 60° gave six products, the [1,1′-biphenyl]carboxaldehydes **9a**–**9c** and **15**–**17**, which were isolated by silica-gel column chromatography. On the basis of NMR spectroscopy, the first product, **15**, was established to be a $[4+3]\pi$ adduct of the norcaradiene valence isomer of **4**. Two olefinic H-atoms resonated as an *AB* system at δ(H) 5.90 (*dd*, $J = 4.8$, 2.2 Hz) and 5.64 (*dd*, $J = 4.8$, 2.0 Hz). The CH_2 group of the cyclopropane moiety gave rise to a *md* at δ(H) 1.80 ($J = 12.5$ Hz). Furthermore, the ^{13}C-NMR spectrum showed 16 C-signals (two overlapped, *i.e.*, 18 signals), and the molecular-ion peak appeared at *m/z* 266 (M^+) confirming the structure of **15**.

The $[6+3]\pi$ adduct **16** of **7** and **5** had an ^{1}H-NMR spectrum very similar to that of $[6+3]\pi$ adduct **11** derived from the reaction of methyl acetoacetate. All spectral data and the molecular-ion peak at *m/z* 266 (M^+) are in agreement with the proposed structure. A similar product and spectral results were obtained by *Balci* and co-workers [13] from the $Mn(OAc)_3$-catalyzed addition of acetylacetone to cyloheptatriene.

The structure of the condensation product **17** of acetylacetone (**7**) with 4-phenylbenzaldehyde (**9c**) was confirmed by the following spectroscopic data: Signals of one olefinic and nine aromatic H-atoms in the ^{1}H-NMR spectrum and of fourteen C-atoms in the ^{13}C-NMR spectrum (eight aromatic C, two olefinic C, two C=O, and two

aliphatic C-atoms). The molecular-ion peak at *m/z* 264 (M^+) was consistent with a symmetrical structure and condensation product.

The reaction of the mixture **4/5** with dimedone (= 5,5-dimethylcyclohexane-1,3-dione; **8**) gave products **18**, **19**, and **20** which were isolated by silica-gel column chromatography. The $[2+3]\pi$ adduct **18** of **4** and **8** had a molecular-ion peak at *m/z* 306 (M^+), consistent with a 1:1 adduct. Its ^{1}H-NMR spectrum showed the signals in agreement with the structure: δ(H) 6.19 (*A* of *AB* (*dd*), $J = 11.7, 7.4$ Hz, H–C(9)), 6.05 (*d*, $J = 7.4$ Hz, H–C(8)), 5.86 (*B* of *AB* (*dd*, $J = 11.7, 5.8$ Hz, H–C(10)), 5.00–4.98 (*m*, H–C(5a)), and 4.00 (*d*, $J = 5.8$ Hz, H–C(10a)). The coupling patterns of the olefinic H-atoms and the allylic H–C(10a) ($J(8,9) = 7.4$ Hz, $J(9,10) = 11.7$ Hz, and $J(10,10a) = 5.8$ Hz) confirmed the structure. The CH_2 group of the cycloheptadiene moiety resonated as *dm* at δ(H) 2.53–2.48 ($J_{gem} = 12.4$ Hz). A similar structure and coupling pattern have been observed by *Takeshita et al.* [14] for the addition product of acenaphthenequinone (= acenaphthylene-1,2-dione) and CHT. Moreover, a similar product and spectral results were obtained by *Südemen et al.* [13] for the $Mn(OAc)_3$-catalyzed addition product of dimedone and CHT.

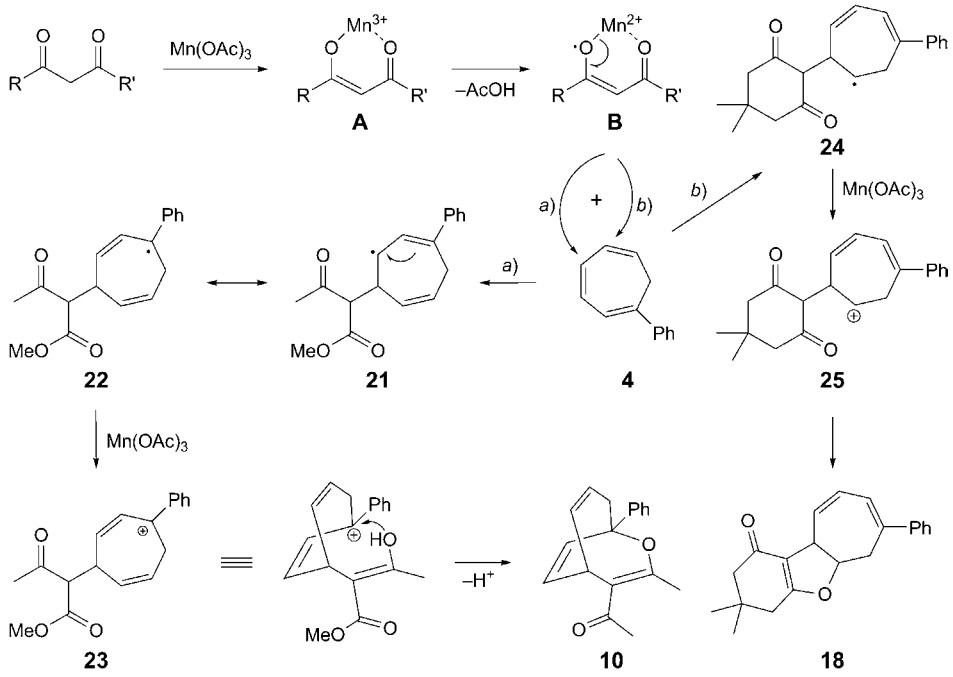
The structure of the $[6+3]\pi$ adduct **19** of **5** and dimedone was derived from the following spectroscopic data: appearance of the signals of three olefinic H-atoms in the ^{1}H-NMR spectrum and only one signal for a C=O group in the ^{13}C-NMR spectrum as well as the molecular-ion peak at *m/z* 306 (M^+), indicating the presence of a 1:1 adduct ($[6+3]\pi$ adduct). The olefinic H-atoms resonated as a *m* at δ(H) 6.26–6.22. The spectrum was very similar to that of compound **11**. Additionally, a similar product and spectral results were obtained by *Balci* and co-workers [13] for the $Mn(OAc)_3$-catalyzed addition of dimedone to CHT.

The norcaradiene-type adduct **20**, in analogy to the $[4+3]\pi$ adduct **15** from **4/5** with **7**, showed olefinic H-atoms resonating as *AB* system at δ(H) 5.94 (*dd*, $J = 5.2, 2.0$ Hz) and 5.56 (*dd*, $J = 5.2, 2.4$ Hz). The cyclopropane moiety gave rise to a broad *d* at δ(H) 3.37 ($J = 5.5$ Hz, 2 H), a *dt* at δ(H) 1.78 ($J = 13.6, 2.0$ Hz, 1 H), and a broad *d* at δ(H) 1.10 ($J = 5.2$ Hz, 1 H). This data and the molecular-ion peak at *m/z* 306 (M^+) were in accordance with the structure. In addition, the ^{1}H-NMR spectrum of **20** was very similar to that of compound **15**.

The rearrangement products **9a**–**9c** were not detected in the reaction with dimedone (**8**) since the reaction rate of dimedone (conversion after 5 min) was faster than that of methyl acetoacetate (**6**; conversion after 30 min) and acetylacetone (**7**; conversion after 3 h).

The mechanism of the formation of $[4+3]\pi$ adduct **10** and $[2+3]\pi$ adduct **18** from **4** can be explained as shown in *Scheme 2*. After formation of [Mn^{III}(enolato)] complex **A** from $Mn(OAc)_3$ and the 1,3-dicarbonyl compound [12], Mn^{3+} is reduced to Mn^{2+} resulting in the resonance-stabilized radical intermediate **B**. Radical **B** is then added to C(4) of 1-phenylcyclohepta-1,3,5-triene (**4**) resulting in **21** which is mesomeric with the more stable benzylic radical **22**. This radical is oxidized to the carbocation **23** with $Mn(OAc)_3$. Then, the intramolecular cyclization can lead to product **10**, which represents the $[4+3]\pi$ adduct. Addition of intermediate **B** to C(5) of **4** gives the radical **24**, which is oxidized to carbocation **25**. The latter affords the $[2+3]\pi$ adduct **18** by cyclization.

Scheme 2

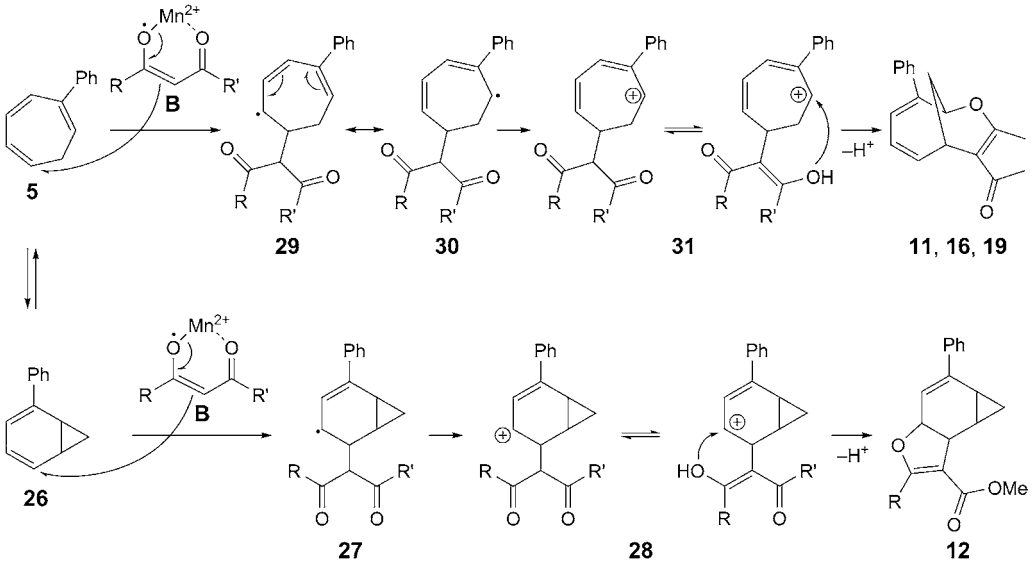


Addition of intermediate **B** to C(5) of the norcaradiene valence isomer **26** of 2-phenylcyclohepta-1,3,5-triene (**5**) results in the formation of radical **27**, which is oxidized to carbocation **28**. The cyclization of carbocation **28** leads to the $[2+3]\pi$ adduct **12** (*Scheme 3*). Addition of radical intermediate **B** to C(6) of **5** gives the mesomeric radicals **29** and **30**. Oxidation of the latter to carbocation **31** followed by cyclization gives rise to $[6+3]\pi$ adducts **11**, **16**, and **19** (*Scheme 3*).

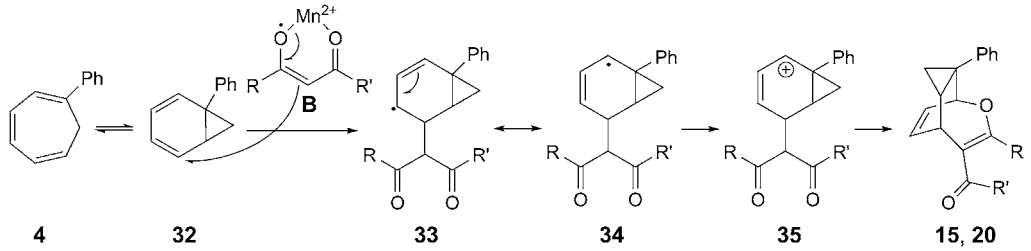
Finally, addition of intermediate **B** to C(5) of norcaradiene valence isomer **32** of 1-phenylcyclohepta-1,3,5-triene (**4**) gives the allyl radicals **33**/**34**. Oxidation leads to carbocation **35**, which cyclizes to the $[4+3]\pi$ adducts **15** and **20** (*Scheme 4*).

Conclusions. – We examined the manganese(III) acetate catalyzed oxidative radical-addition reactions of methyl acetoacetate (**6**), acetylacetone (**7**), and dimedone (**8**) to 1- and 2-phenylcyclohepta-1,3,5-triene (**4** and **5**). It was found that the reactions of 1-phenylcycloheptatriene **4** were slower than those of 2-phenylcycloheptatriene **5**. The $[2+3]$ and $[4+3]$ dihydrofuran addition products of type **2** such as **18** and **10**, respectively, derived from the cycloheptatriene structure, and the $[4+3]$ dihydrofuran addition products of type **1** such as **15** and **20**, derived from the norcaradiene structure, were obtained from **4**. The $[6+3]$ dihydrofuran addition products of type **3** such as **11**, **16**, and **19**, derived from the cycloheptatriene structure, and the $[4+3]$ dihydrofuran addition product **12**, derived from the norcaradiene structure, were obtained from **5**. The 1:2 adducts **13** and **14** were obtained from the reaction of methyl acetoacetate (**6**).

Scheme 3



Scheme 4



In case of the methyl acetoacetate and acetylacetone (**7**), the rearrangement products **9a**–**9c** and condensation product **17** were isolated.

The authors are indebted to the Department of Chemistry (Gaziosmanpasa University), to Prof. Dr. *Hasan Seçen* (Atatürk University) for fruitful discussions, and to Dr. *Ebru Mete*, Hatice Seçinti, for recording mass spectra.

Experimental Part

1. *General.* Thin layer chromatography (TLC): silica gel *60 GF*$_{254}$ (*Merck*). Column chromatography (CC): silica gel *60* (0.063–0.200 mm; *Merck*). M.p.: *Electrothermal 9100* apparatus. IR Spectra (KBr or liq.): *Jasco-430* FT/IR spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectrum: *Bruker-Avance-III* instrument; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, J in Hz. MS: *Thermofinnigan Trace GC/Trace DSQ/A1300* (quadrupol, EI (70 eV)) equipped with a *SGE-BPX5* MS cap. column (30 m × 0.25 mm i.d.; 0.25 μm); in *m/z* (rel. %). Elemental analyses: *LECO-CHNS-932* elemental analyzer.

2. *Reaction of* **4**/**5** *with 1,3-Dicarbonyl Compounds: General Procedure.* A mixture of $Mn(OAc)_3$ (6.4 g, 23.6 mmol) in AcOH (15 ml) was heated under N_2 at 80° until it dissolved and then cooled to 60°. A soln. of **4**/**5** (1.0 g, 5.9 mmol) and 1,3-dicarbonyl derivative (23.6 mmol) in AcOH (5 ml) was added to this mixture. The reaction was finished when the dark brown color of the soln. disappeared. Then AcOH was evaporated, H_2O (10 ml) added to the residue, and the mixture extracted with AcOEt (3 × 20 ml). The combined org. phase was neutralized with sat. $NaHCO_3$ soln., dried (anh. Na_2SO_4), and concentrated. The crude products were separated and purified by CC (SiO_2, hexane/AcOEt) or prep. TLC (SiO_2 (20 × 20 cm plates, 2 mm thickness), using hexane/AcOEt 9:1).

3. *Reaction of Methyl Acetoacetate* (**6**) *with* **4**/**5**. After completion of the reaction (30 min), the crude products were separated by CC (silica gel hexane/AcOEt 9:1): [1,1′-biphenyl]carboxaldehydes **9a**–**9c** (45 mg, 4%; colorless liquid) and **10**–**14**, in this order.

Methyl 3-Methyl-1-phenyl-2-oxabicyclo[3.3.2]deca-3,6,9-triene-4-carboxylate (**10**): Yield 165 mg (10%). Yellowish liquid. IR (KBr): 3060, 3021, 2950, 2850, 1697, 1649, 1490, 1436, 1226, 1099, 989, 752, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.32–7.29 (*m*, 5 H); 6.31 (*ddd*, *J* = 12.0, 8.4, 5.6, H–C(9)); 6.12 (*dd*, *J* = 12.0, 2.0, H–C(10)); 6.09 (*d*, *J* = 12.0, H–C(7)); 5.89 (*dd*, *J* = 12.0, 5.6, H–C(6)); 3.68 (*s*, MeO); 3.41 (*d*, *J* = 2.4, H–C(5)); 2.47 (*ddd*, *J* = 20.0, 9.6, 2.0, H–C(8)); 2.38 (*s*, Me–C(3)); 2.32 (*ddd*, *J* = 20.0, 9.6, 2.0, H–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 166.3; 165.9; 144.6; 135.8; 134.0; 128.2; 127.4; 127.3; 124.3; 124.2; 106.7; 93.6; 61.7 50.7; 30.4; 14.2. MS: 282 (20, M^+), 250 (45), 235 (25), 207 (100), 179 (90), 165 (85), 152 (38). Anal. calc. for $C_{18}H_{18}O_3$ (282.13): C 76.57, H 6.43; found: C 76.77, H 6.24.

*Methyl (1*RS*,6*RS*)-8-Methyl-5-phenyl-7-oxabicyclo[4.3.1]deca-2,4,8-triene-9-carboxylate* (**11**): Yield 245 mg (14%). Yellowish liquid. IR (KBr): 3060, 3021, 2950, 2850, 1704, 1639, 1436, 1253, 1211, 1087, 755, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55 (br. *d*, *J* = 7.6, 2 H); 7.37–7.24 (*m*, 3 H); 6.26–6.21 (*m*, 3 olef. H); 5.15 (*d*, *J* = 9.2, H–C(6)); 3.78 (*s*, MeO); 3.43 (*t*, *J* = 10.2, H–C(1)); 2.91 (*d*, *J* = 13.6, H–C(10a)); 2.52 (*t*, *J* = 12.0, H–C(10b)); 2.26 (*s*, Me–C(8)); data in good agreement with those given in [13]. ^{13}C-NMR (100 MHz, $CDCl_3$): 167.9; 166.2; 145.4; 142.2; 130.1; 128.5 (2 C); 128.1; 126.3; 125.8 (2 C); 122.7; 106.7; 71.13; 50.84; 34.7; 33.52; 14.23. MS: 282 (14, M^+), 250 (32), 207 (100), 179 (58), 165 (36), 152 (18), 142 (28), 115 (28), 103 (10). Anal. calc. for $C_{18}H_{18}O_3$ (282.13): C 76.57, H 6.43; found: C 76.34, H 6.56.

*Methyl (3a*RS*,5a*SR*,6a*RS*,6b*RS*)-3a,5a,6a,6b-Tetrahydro-2-methyl-5-phenyl-6a*H*-cyclopropa[e]benzofuran-1-carboxylate* (**12**): Yield 275 mg (16%). Yellowish liquid. IR (KBr): 3060, 3021, 2950, 2927, 1685, 1635, 1440, 1249, 1222, 1083, 752, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57 (br. *d*, *J* = 7.2, 2 H); 7.40–7.29 (*m*, 3 H); 5.74 (*d*, *J* = 4.0, H–C(4)); 4.97 (*dd*, *J* = 10.8, 4.0, H–C(3a)); 3.83 (*d*, *J* = 10.8, H–C(6b)); 3.78 (*s*, MeO); 2.26 (*s*, Me–C(2)); 1.77 (*dd*, *J* = 13.2, 8.4, H–C(5a)); 1.66 (*ddd*, *J* = 12.5, 8.4, 4.8, H–C(6)); 1.27 (*ddd*, *J* = 12.5, 8.4, 4.8, H–C(6)); 0.22 (*dd*, *J* = 10.4, 4.4, H–C(6a)). ^{13}C-NMR (100 MHz, $CDCl_3$): 167.96; 166.7; 144.4; 140.6; 128.4 (2 C); 127.9; 125.8 (2 C); 115,1; 105.9; 76.7; 50.8; 38.4; 18.5; 14.8; 13.4; 11.8. MS: 282 (13, M^+), 250 (98), 232 (35), 222 (55), 207 (100) 179 (98), 167 (90), 152 (40). Anal. calc. for $C_{18}H_{18}O_3$ (282.13): C 76.57, H 6.43; found: C 76.83, H 6.52.

*Dimethyl (6*RS*,10*RS*)-3a,6,10,10a-Tetrahydro-2,8-dimethyl-5-phenyl-6,10-methanofuro[2,3-*e*]oxonin-3,9-dicarboxylate* (**13**): Yield 205 mg (12%). Yellowish liquid. IR (KBr): 3060, 3021, 2950, 2854, 1727, 1623, 1436, 1245, 1083, 977, 755, 701. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.44 (*m*, 2 H); 7.27–7.21 (*m*, 3 H); 5.45 (*d*, *J* = 5.0, H–C(4)); 5.19 (*dd*, *J* = 12.6, 6.0, 1 H); 4.91 (*d*, *J* = 7.6, 1 H); 3.78 (*s*, MeO); 3.75 (*s*, MeO); 2.42 (*d*, *J* = 13.6, 1 H); 2.26 (*s*, Me–C(8)); 2.24 (*s*, Me–C(2)); 2.16 (*d*, *J* = 5.6, 1 H); 2.12 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.9; 167.6; 165.8; 164.7; 143.6; 129.8; 127.6; 127.0; 123.1; 104.4; 103.5; 82.1; 74.1; 51.1; 50.1 34.8; 27.3; 26.5; 20.3; 14.9. MS: 396 (5, M^+), 364 (8), 280 (20), 247 (15), 219 (8), 200 (25) 179 (98), 165 (23), 153 (100), 141 (15), 115 (13). Anal. calc. for $C_{23}H_{24}O_6$ (396.16): C 69.68, H 6.10; found: C 69.54, H 6.32.

*Dimethyl (4*RS*,8*SR*)-3a,4,8,10a-Tetrahydro-2,6-dimethyl-9-phenyl-4,8-methanofuro[2,3-*e*]oxonin-3,5-dicarboxylate* (**14**): Yield 138 mg (8%). Yellowish liquid. IR (KBr): 3064, 3023, 2952, 2851, 1730, 1628, 1439, 1247, 1086, 979, 758, 704. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.19 (*m*, 5 H); 6.20 (*dd*, *J* = 11.6, H–C(10)); 5.55 (*dd*, *J* = 11.6, 1.6, H–C(10a)); 5.29 (br. *d*, *J* = 10.0, 1 H); 3.82 (*s*, MeO); 3.75 (*s*, MeO); 2.92 (*dd*, *J* = 11.2, 5.6, 1 H); 2.51–2.38 (*m*, 1 H); 2.35–2.26 (*m*, 1 H); 2.18 (*s*, Me–C(6)); 2.12–2.10 (*m*, 1 H); 2.04 (*s*, Me–C(2)). ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3; 168.06; 166.218; 165.8; 138.4; 128.8; 128.4; 128.1; 127.7; 127.5; 105.8 ; 83.3; 52.5; 51.6; 43.7; 43.3; 32.2; 26.0; 14.3. MS: 396 (2, M^+), 279 (8), 167 (75), 149 (100), 113 (23). Anal. calc. for $C_{23}H_{24}O_6$ (396.16): C 69.68, H 6.10; found: C 70.17, H 6.23.

4. *Reaction of Acetylacetone* (**7**) *with* **4**/**5**. After completion of the reaction (3 h) the crude products was were separated by CC (silica gel, hexane/AcOEt 9:1): *[1,1′-biphenyl]carboxaldehydes* **9a**–**9c** (150 mg, 14%; colorless liquid) and **15**–**17**, in this order.

*1-[(1*RS,*2*SR,*4*SR,*5*SR*)-7-Methyl-4-phenyl-6-oxatricyclo[3.3.2.0^{2,4}]deca-7,9-dien-8-yl]ethanone* (**15**): Yield 230 mg (18%). Yellowish liquid. IR (KBr): 3060, 3014, 2927, 2854, 1714, 1679, 1596, 1361, 1236, 939, 752, 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.34 (*m*, 5 arom. H); 5.90 (*dd*, *J* = 4.8, 2.2, H–C(9 or 10)); 5.64 (*dd*, *J* = 4.8, 2.0, H–C(9 or 10)); 3.87–3.85 (*m*, H–C(5)); 3.38–3.35 (*m*, 2 H); 2.39–2.34 (*m*, 1 H); 2.32 (*s*, MeCO–C(8)); 2.24 (*m*, Me–C(7)); 1.80 (*dm*, *J* = 12.5, H–C(2)). ^{13}C-NMR (100 MHz, $CDCl_3$): 194.54; 168.68; 138.02; 132.53; 131.44; 127.94; 127.79; 126.12; 116.54; 95.28; 53.15; 52.42; 49.28; 35.41; 29.50; 15.47. MS: 266 (8, M^+), 221 (30), 203 (100), 165 (95), 152 (20). Anal. calc. for $C_{18}H_{18}O_2$ (266.13): C 81.17, H 6.81; found: C 81.36, H 6.73.

*1-[(1*RS,*6*SR*)-8-Methyl-5-phenyl-7-oxabicyclo[4.3.1]deca-2,4,8-trien-9-yl]ethanone* (**16**): Yield 200 mg (16%). Yellowish liquid. IR (KBr): 3056, 3021, 2921, 2854, 1714, 1671, 1357, 1232, 1072, 950, 752, 700.^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (*d*, *J* = 7.6, 2 H); 7.37 (*t*, *J* = 8.0, 2 H); 7.25 (*t*, *J* = 7.2, 1 H); 6.25–6.20 (*m*, 3 olef. H); 5.06 (*d*, *J* = 8.8, H–C(6)); 3.46 (*t*, *J* = 10.4, H–C(1)); 2.82 (br. *d*, *J* = 12.8, H–C(10)); 2.45 (br. *d*, *J* = 10.4, H–C(10)); 2.31 (*s*, MeCO); 2.26 (*m*, Me–C(8)); data in good agreement with those given in [13]. ^{13}C-NMR (100 MHz, $CDCl_3$): 193.63; 167.18; 145.78; 141.97; 129.43; 128.58; 128.54; 127.40; 126.04; 125.96; 122.53; 85.58; 52.02; 33.42; 29.16; 15.49. MS: 266 (8, M^+), 221 (33), 203 (100), 178 (45), 165 (98), 152 (15). Anal. calc. for $C_{18}H_{18}O_2$ (266.13): C 81.17, H 6.81; found: C 81.69, H 6.98.

3-([1,1′-Biphenyl]-4-ylmethylene)pentane-2,4-dione (**17**): Yield 250 mg (20%). Yellowish crystals. M.p. 87–89°. IR (KBr): 3060, 3020, 2923, 2850, 1708, 1654, 1602, 1382, 1245, 1172, 1001, 835, 759, 694. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (*t*, *J* = 8.6, 4 arom. H); 7.53 (*s*, 1 olef. H); 7.48 (*t*, *J* = 8.4, 4 arom. H); 7.41 (*t*, *J* = 7.4, 1 arom. H); 2.46 (*s*, Me); 2.36 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 205.76; 196.44; 143.46; 142.54; 139.68; 139.38; 131.72; 130.35; 128.98; 128.14; 127.63; 127.07; 31.74; 26.52. MS: 264 (100, M^+), 249 (38), 221 (65), 207 (98), 178 (96), 165 (88), 152 (43), 115 (10). Anal. calc. for $C_{18}H_{16}O_2$ (264.12): C 81.79, H 6.10; found: C 81.49, H 6.38.

5. *Reaction of Dimedone* (**8**) *with* **4**/**5**. After completion of the reaction (5 min) the crude product was filtered through a short silica-gel column with hexane/AcOEt 9:1 which separated unreacted 1-phenylcyclohepta-1,3,5-triene (**4**; 0.15 g). Then, filtration was continued with hexane/AcOEt 1:1 which separated the addition products (0.8 g, total yield 51% rel. to 0.85 g of starting CHT **4**/**5**. The addition products (0.8 g) were subjected to CC (silica gel, hexane/AcOEt 7:3): **18**–**20**, in this order.

*(5a*RS,*10a*RS*)-2,3,4,5a,6,10a-Hexahydro-3,3-dimethyl-7-phenyl-1*H*-benzo[*b*]cyclohepta[*d*]furan-1-one* (**18**): Yield 200 mg (13% and 59% rel. to CHT **4**). Colorless liquid. IR (KBr): 3060, 3018, 2958, 2927, 2869, 1648, 1612, 1382, 1076, 1029, 755, 696. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.56 (*d*, *J* = 7.7, 2 arom. H); 7.37 (*t*, *J* = 7.4, 2 arom. H); 7.28 (*t*, *J* = 7.4, 1 arom. H); 6.19 (*dd* (*A* of *AB*), *J* = 11.7, 7.4, H–C(9)); 6.05 (*d*, *J* = 7.4, H–C(8)); 5.86 (*dd* (*B* of *AB*), *J* = 11.7, 5.9, H–C(10); 5.00–4.98 (*m*, 1 H); 4.00 (br. *d*, *J* = 5.9, H–C(10a)); 2.53–2.48 (*dm*, *J* = 12.4, 2 H–C(6)); 2.28–2.02 (*m*, 4 H); 1.07 (*s*, Me–C(3)); 1.03 (*m*, Me–C(3)); data in good agreement with those given in [13]. ^{13}C-NMR (100 MHz, $CDCl_3$): 197.6; 168.5; 149.9; 144.3; 129.4; 128.1 (2 C); 127.8; 126.9; 126.7 (2 C); 121.8; 112.7; 72.1; 50.8; 42.5; 32.1; 31.9; 29.37; 28.8; 27.1. MS: 306 (5, M^+), 293 (10), 252 (100), 194 (50), 154 (85), 115 (70). Anal. calc. for $C_{21}H_{22}O_2$ (306.16): C 82.32, H 7.24; found: C 82.12, H 7.43.

*(2*RS,*7*SR*)-7,9,10,11-Tetrahydro-10,10-dimethyl-3-phenyl-2,7-methano-1-benzoxonin-8(2*H*)-one* (**19**): Yield 150 mg (10% and 12% rel. to CHT **4**). Yellowish liquid. IR (KBr): 3018, 2958, 2935, 2873, 1714, 1623, 1394, 1373, 1216, 1037, 752, 700, 665. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (*d*, *J* = 7.2, 2 arom. H); 7.34 (*t*, *J* = 7.4, 2 arom. H); 7.26 (*t*, *J* = 7.2, 1 arom. H); 6.26–6.22 (*m*, 3 olef. H); 5.28 (*d*, *J* = 9.3, H–C(2)); 3.56 (*t*, *J* = 10.2, H–C(7)); 3.03 (*d*, *J* = 12.8, H–C(12)); 2.42 (*t*, *J* = 12.8, H–C(12)); 2.31–2.14 (*m*, 4 H); 1.13 (*s*, Me–C(10)); 1.10 (*m*, Me–C(10)); data in good agreement with those given in [13]. ^{13}C-NMR (100 MHz, $CDCl_3$): 194.57; 175.10; 145.62; 143.27; 129.79; 128.54; 128.36; 127.47; 125.93; 122.73; 115.71; 87.58; 51.08; 50.06; 37.64; 34.17; 32.66; 29.19; 28.10. MS: 306 (15, M^+), 293 (100), 222 (10), 191 (48), 179 (16), 165 (55), 114 (20), 105 (43). Anal. calc. for $C_{21}H_{22}O_2$ (306.16): C 82.32, H 7.24; found: C 82.54, H 7.52.

*(1a*RS,*2*RS,*8*SR,*8a*RS*)-1,1a,2,4,5,6,8,8a-Octahydro-5,5-dimethyl-1a-phenyl-2,8-etheno-7*H*-cyclopropa[*c*][1]benzoxepin-7-one* (**20**): Yield 450 mg (28% and 35% rel. to CHT **4**). Yellowish iquid. IR (KBr): 3060, 3010, 2958, 2927, 2869, 1714, 1619, 1401, 1232, 1135, 790, 759, 696. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.27 (*m*, 5 arom. H); 5.94 (*dd*, *J* = 5.2, 2.0, 1 olef. H); 5.56 (*dd*, *J* = 5.2, 2.4, 1 olef. H); 3.89 (*m*, 1 H); 3.37 (br. *d*, *J* = 5.5, 2 H); 2.46–2.21 (*m*, 4 H); 1.78 (*dt*, *J* = 13.6, 2.0, 1 H); 1.10 (br. *d*, *J* = 5.2, 1 H); 1.18 (*s*, Me–C(5)); 1.07 (*s*, Me–C(5)). ^{13}C-NMR (100 MHz, $CDCl_3$): 194.82; 176.69; 137.47; 132.01; 131.98; 128.39; 127.96; 126.37; 116.28; 99.92; 51.60; 51.08; 49.51; 48.73; 38.17; 35.42; 34.20; 28.83; 28.61. MS: 306 (6, M^+), 292 (4), 240 (100), 184 (98), 156 (95). Anal. calc. for $C_{21}H_{22}O_2$ (306.16): C 82.32, H 7.24; found: C 82.48, H 7.05.

REFERENCES

[1] G. Bar, A. F. Parsons, C. B. Thomas, *Chem. Commun*. **2001**, 1350.
[2] M. Yilmaz, E. Bicer, A. T. Pekel, *Turk. J. Chem*. **2005**, *29*, 579.
[3] R. Çalışkan, T. Pekel, W. H. Watson, M. Balci, *Tetrahedron Lett*. **2005**, *46*, 6227.
[4] M. Yılmaz, A. T. Pekel, *Synth. Commun*. **2001**, *31*, 3871.
[5] Z. Zhang, G.-W. Wang, C.-B. Miao, Y.-W. Dong, Y.-B. Shen, *Chem. Commun*. **2004**, 1832.
[6] M. Yılmaz, A. T. Pekel, *Synth. Commun*. **2001**, *31*, 2189.
[7] M. Ceylan, E. Fındık, *Synth. Commun*. **2008**, *38*, 1070.
[8] H. Tsuruta, K. Tomisawa, T. Mukai, *Bull. Chem. Soc. Jpn*. **1972**, *45*, 1584.
[9] Y. Ohnishi, Y. Akasaki, A. Ohno, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3307.
[10] M. Ceylan, E. Fındık, H. Seçen, *Helv. Chim. Acta.* **2008**, *91*, 559.
[11] T. Asao, M. Yagihara, Y. Kitahara, *Bull. Chem. Soc. Jpn*. **1978**, *51*, 2131.
[12] A. Mori, H. Takeshita, *Bull. Chem. Soc. Jpn*. **1985**, *58*, 1581.
[13] M. B. Südemen, M. Zengin, H. Genç, M. Balci, *Turk. J. Chem.* **2010**, *35*, 1.
[14] H. Takeshita, A. Mori, M. Funakura, H. Mametsuka, *Bull. Chem. Soc. Jpn*. **1977**, *50*, 315.

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