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Reaction of cycloheptatriene derivatives with 1,3-diketones in the presence of $Mn(OAc)_3$

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The reactions of some 1,3-dicarbonyl compounds with cycloheptatriene derivatives in the presence of $Mn(OAc)_3$ were examined. Cycloheptatriene forms mainly [2+3] and [6+3] dihydrofuran addition products derived from cycloheptatriene. However, the reaction of acetylacetone with cycloheptatriene substituted with an electron withdrawing group exclusively gave products derived from the norcaradiene structure. The formation mechanism of the products as well as the role of the substituent attached to cycloheptatriene is discussed.

Key Words: Cycloheptatriene, norcaradiene, manganese(III) acetate, 1,3-dicarbonyl compounds, radicals

Introduction

Cycloheptatriene undergoes 2 dynamic processes; valence isomerization and ring inversion.[1] The unsubstituted cycloheptatriene (CHT) is in equilibrium with the energetically higher norcaradiene (NCD) tautomer (Scheme 1).

Electron-accepting substituents (**X**) such as CHO, COOR, and CN at C-7 tend to shift the equilibrium to the norcaradiene (**2**) side, while π-electron-donating substituents such as OR and NR_2 favor the cycloheptatriene structure.[1]

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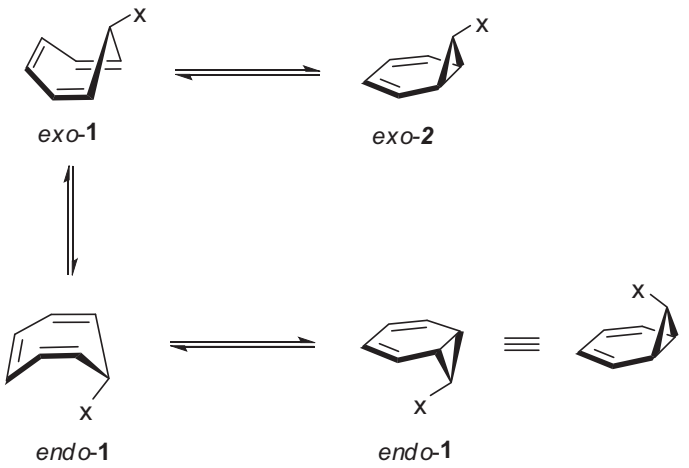
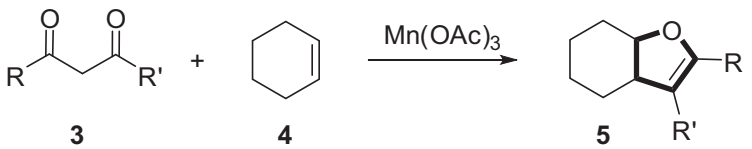


Scheme 1

Hoffmann,[2] Günther,[3] and Tang et al.[4] explained this phenomenon on the basis of HOMO and LUMO interactions between the cyclopropane ring and substituents. It has been shown by our group[5] and others[6] that singlet oxygen and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) are sufficiently reactive to intervene in the cycloheptatriene-norcaradiene equilibrium via cycloaddition. Thus, ratios of cycloheptatriene and norcaradiene endoperoxides qualitatively reflect the distribution of the valence isomers in the 7-substituted cycloheptatrienes.



Scheme 2

In this paper, we describe the reaction of some 1,3-dicarbonyl compounds **3** in the presence of $Mn(OAc)_3$ with cycloheptatriene. Heiba, Dessau, Bush, and Finkbeiner have demonstrated that $Mn(OAc)_3$ in acetic acid converts olefins to γ-lactons.[7] Activated carbonyl groups (1,3-dicarbonyl compounds) can also add to a double bond to form dihydrofuran derivatives **5**[8] (Scheme 2).[9] We were interested in addressing the question of whether the reaction of 1,3-dicarbonyl compounds in the presence of $Mn(OAc)_3$ can intervene in the cycloheptatriene-norcaradiene equilibrium to form dihydrofuran-fused cycloheptatriene and norcaradiene derivatives.

Experimental

General: Melting points are uncorrected. Infrared spectra were obtained from KBr pellets on an FT-IR Bruker Vertex 70 instrument. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker-Biospin (DPX-400) instrument. 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 aluminum plates. Elemental analyses were carried out on a Leco-932 model CHNS analyzer.

Reaction of cycloheptatriene (6) with acetylacetone in the presence of $Mn(OAc)_3/Cu(OAc)_2$: 7.24 g (27 mmol) of $Mn(OAc)_3.2H_2O$ and 0.546 g (3 mmol) of $Cu(OAc)_2$ were dissolved in 100 mL of acetic acid. A mixture of 0.92 g (10 mmol) of cycloheptatriene **6** and 1.0 g (10 mmol) of acetylacetone was prepared in 50 mL of acetic acid and added to the metal oxidant solution dropwise under nitrogen atmosphere over 30 min. The reaction was stirred at 80 °C for 12 h. After the completion of the reaction, the mixture was extracted with CH_2Cl_2 and water; then the organic phase was washed with saturated Na_2CO_3. After the organic extracts were dried over $CaCl_2$ the solvent was removed to give the crude product, which was then chromatographed on silica gel (50 g) eluting with n-hexane/EtOAc (9:1) to give in the following order: 0.076 g of **9**, 0.95 g of **7,** and 0.77 g of **8** with yields of 50%, 41%, and 4.4%, respectively.

1-[(1*R*,6*S*)-8-methyl-7-oxabicyclo[4.3.1]deca-2,4,8-trien-9-yl]ethanone (9): ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.25 (dd, $J_{2,3}$ = 10.8 and $J_{2,1}$ = 8.6 Hz, H-2), 5.73 (dd, $J_{4,5}$ = 10.8 and $J_{4,3}$ = 7.1 Hz, H-4), 5.94 (ddd, $J_{5,4}$ = 11.8, $J_{5,6}$ = 6.9, and $J_{5,10}$ = 0.5 Hz, H-5), 5.81 (dd, $J_{3,2}$ = 11.8 and $J_{3,4}$ = 6.1 Hz, H-3), 4.81 (ddt, $J_{1,2}$ = 8.6, $J_{1,10a}$ =4.1 and $J_{1,10b}$ = 1.7 Hz, H-1), 3.54 (br t, J = 6.9 Hz, H-6), 2.20 (s, 3H), 2.15 (m, H-10a), 2.11 (d, J =1.3 Hz, 3H), 1,86 (ddd, $J_{10a,10b}$ = 13.9, $J_{10b,1}$ = 1.7 and $J_{10b,6}$ = 1.3 Hz, H-10b). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 198.7, 163.0, 138.2, 130.0, 128.9, 124.3, 114.6, 71.3, 32.5, 31.4, 27.7, 21.0. IR (KBr, cm^{-1}) 2940, 2920, 1710, 1680, 1600, 1557, 1330, 1306, 1240, 1211, 1166, 1070, 1047, 912, 705. Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.451; H, 7.35.

***rel*-(3a*S*,8a*S*)-1-(2-methyl-4,8a-dihydro-3a*H*-cyclohepta[b]furan-3-yl) ethanone (7):** Colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.09 (dd, J = 9.8 and 5.4 Hz, 1H), 6.05 (dd, J = 11.9 and 2.9 Hz, 1H), 5.95 (dd, J = 11.9 and 5.3 Hz, 1H), 5.88 (ddd, J = 9.8, 1.2 and 5.3 Hz, 1H), 4.92 (br d, J = 8.6 Hz, 1H), 3.18 (br t, J = 10.0 Hz, 1H), 2.21 (m, 1H), 2.18 (s, 3H), 2.16 (d, J = 0.9 Hz, 3H), 1.92 (dt, J =5.4 and 1.2 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 193.1, 166.9, 134.5, 129.9, 127.1, 126.9, 118.1, 84.5, 51.8, 30.0, 29.0, 15.3. IR (KBr, cm^{-1}) 3027, 1699, 1662, 1608, 1387, 1299, 1266.48, 1226, 1202, 945, 711, 678. Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.25.

***rel*-(3a*S*,8a*S*)-1-(2-methyl-8,8a-dihydro-3a*H*-cyclohepta[b]furan-3-yl)ethano-ne (8):** Colorless liquid;^{1}H-NMR (400 MHz, benzene-d_6)δ 6.19 (dd, $J_{4,5}$ = 11.2 and $J_{4,3a}$ = 3.5 Hz, H-4), 5.98 (dd, $J_{6,7}$ = 10.2 and $J_{6,5}$ = 4.4 Hz, H-6), 5.90 (ddd, $J_{4,5}$ = 11.2, $J_{5,6}$ = 4.4 and $J_{5,3a}$ = 2.5 Hz, H-5), 5.82 (dt, $J_{7,6}$ = 10.2 and $J_{7,8}$ = 7.8 Hz, H-7), 4.66 (dt, $J_{8a,3a}$ = = 10.5 and $J_{8a,8}$ = 7.8 Hz, H-8a), 3.71 (br d, $J_{3a,8a}$ = 10.5 Hz, H-3a), 2.42 (t, $J_{8,8a}$ = $J_{8,7}$ = 7.8 Hz, H-8) 2.04 (s, 3H), 2.00 (d, $J_{CH3,3a}$ =1.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 192.2, 167.3, 136.9, 131.0, 127.6, 127.3, 117.0, 92.9, 46.1, 31.6, 29.1, 14.8. IR (KBr, cm^{-1}) 3023, 1690, 1640, 1412, 1337, 965, 623, 500.

Reaction of cycloheptatriene (6) with dimedone in the presence of $Mn(OAc)_3$: 7.24 g (27 mmol) $Mn(OAc)_3.2H_2O$ and 0.126 g (3 mmol) LiCl were dissolved in 100 mL of acetic acid and to this solution was added a mixture of 0.92 g (10 mmol) of cycloheptatriene **(6)** and 1.4 g of dimedone **14** (10 mmol) in 50 mL of acetic acid dropwise under nitrogen atmosphere over 30 min. The reaction was stirred at 80 °C for 30 min. After the completion of the reaction the mixture was extracted with CH_2Cl_2 and water. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with saturated Na_2CO_3 and dried over $CaCl_2$. The solvent was removed and the residue was chromatographed on silica gel (50 g) eluting with n-hexane/EtOAc (9:1) to give the products **17** (101 mg) and **15** (1.89 g) in 4.4% and 82% yields, respectively.

***rel*-(2*S*,7*R*)-10,10-dimethyl-7,9,10,11-tetrahydro-2,7-methano-1-benzoxonin-8(2*H*)-one (17):** White solid, mp 84.0-84.5 °C from ethyl acetate/hexane. ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.35 (dd, $J_{6,5}$ = 11.0 Hz, and $J_{6,7}$ = 8.3 Hz, H-6), 5.92 (dd, $J_{4,3}$ = 11.8 and $J_{4,5}$ = Hz 7.3 H-4), 5.79 (dd, $J_{3,4}$ = 11.8 and $J_{3,2}$ = 6.2 Hz, H-3), 5.67 (dd, $J_{5,6}$ = 11.0 and $J_{5,4}$ = 7.3 Hz, H-5), 4.89 (m, H-2), 3.39 (br t, H-7), 2,19-2.14 (m, H-12'), 2.15 (s, -CH_2-), 2.09 ((AB-system, J = 16.2 Hz, -CH_2-) 1.85 (dd, $J_{12,12'}$ = 14.0 and J = 1.0 Hz, H-12"), 0.95 (s, 3H), 0.93 (s, 3H). ^{13}C-NMR (100 MHz, CDCl3) δ 194.7, 166.1, 137.1, 127.6, 126.1, 121.3, 111.2, 70.4, 48.6, 40.3, 30.1, 27.1, 26.1, 25.7, 25.6. IR (KBr, cm^{-1}) 3030.6, 1642.6, 1376.1, 1340.3, 1216.1, 1134.8, 1082.8, 1029.9, 966.9, 731.3, 691.4. Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.40; H, 7.99.

***rel*-(5a*R*,10a*R*)-3,3-Dimethyl-2,3,4,5a,10,10a-hexahydro-1H-benzo[d]cyclohepta[b]furan-1-one (15):** White solid, mp 66.5-67.0 °C from ethyl acetate/hexane. ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.15-6.10 (m, 1H), 6.11 (dd, J =12.0 and 2.7 Hz, 1H), 5.99 (ddd, J = 12.0, 5.4, and 1.8 Hz, 1H), 5.91 (ddd, J = 10.3, 5.4, and 1.3 Hz, 1H), 5.13 (br d, J = 9.2 Hz, H-5a), 3.38 (br t, J = 9.2 Hz, H-10a) 2.45 (ddd, J = 13.4, 8.3, and 2.0 Hz, H-10'), 2.24 (s, -CH_2-), 2.16 (AB-system, -CH_2-), 1.89 (dddd, J =13.4, 11.5, 5.3, and 1.9 Hz, H-10"), 1.05 (s, 3H), 1.02 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 194.6, 175.0, 134.8, 130.1, 127.7, 127.2, 115.7, 87.5, 51.2, 50.2, 37.7, 34.1, 29.4, 29.2, 27.0. IR (KBr, cm^{-1}) 2970, 1614.0, 1399, 1366, 1223, 1166, 1133, 1036, 959, 912, 887, 839, 716, 687. Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.67; H, 7.45.

Synthesis of 3,3-dimethyl-2,3,4,5a,6,10a-hexahydro-1*H*-benzo[*b*]cyclohepta- [*d*]furan-1-one (16): 0.46 g (2 mmol) of **15** was heated at 80 °C in AcOH for 24 h. After the completion of the reaction, the mixture was extracted with CH_2Cl_2 and water; then the organic phase was washed with saturated Na_2CO_3. After the organic extracts were dried over $CaCl_2$, the solvent was removed to give an isomeric mixture consisting of **15** and **16** in a ratio of 48:52: The isomeric mixture was separated by chromatography on silica gel (50 g) eluting with n-hexane/EtOAc (9:1) to give **15** (193 mg, 42%) and **16** (184 mg, 40%). The isomer **16** was isolated as the second fraction. ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.22 (dd, J =11.4 and 3.4 Hz, 1H), 6.02 (dd, J = 10.1 and 4.8 Hz, 1H), 5.87-5.78 (m, 2H), 4.98 (dt, J =10.4 and 3.5 Hz, 1H), 3.80 (br d, J =10.4 Hz, 1H) 2.51 (ddd, J = 12.4, 7.7, and 3.6 Hz, 1H), 2.20-2.39 (m, 3H), 2.17 (s, 2H), 1.12 (s, 3H), 1.11 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) 194.5, 175.8, 134.0, 131.0, 126.7, 126.5, 114.5, 94.2, 51.3, 43.0, 37.8, 34.0, 31.7, 28.8, 28.4. IR (KBr, cm^{-1}) 3030.6, 1712.6, 1345.6, 1216.1, 976.9, 651.4.

Reaction of 7-cyanocycloheptatriene (18) with acetylacetone in the presence of $Mn(OAc)_3$: 20.6 g (30 mmol) $Mn(OAc)_3.2H_2O$ was dissolved in 200 mL of acetic acid and to this solution was added a mixture of **18** (3.0 g, 25.6 mmol) and acetylacetone (2.56 g, 25.6 mmol) in 50 mL of acetic acid dropwise under nitrogen atmosphere over 30 min. The reaction was stirred at 80 °C for 24 h. After the completion of the reaction, the mixture was extracted with CH_2Cl_2 and water. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with saturated Na_2CO_3 and dried over $CaCl_2$. The solvent was removed to give 4.3 g of crude product. The mixture was chromatographed on silica gel (90 g) eluting with n-hexane/EtOAc (9:1) to give **19**, **20**, **21**, and **22** in that order.

***rel*-(3a*R*,5a*R*,6*R*,6a*S*,6b*R*)-1-acetyl-2-methyl-5a,6,6a,6b-tetrahydro-3a*H*-cyclopropa[3,4] benzo[1,2-*b*]furan-6-carbonitrile (19):** Colorless liquid, 1.54 g (28%). ^{1}**H-NMR** (400 MHz, $CDCl_3$)δ 6.21 (dd, $J_{5,4}$ = 10.2 and $J_{5,5a}$ = 5.0 Hz, H-5), 5.51 (dd, $J_{4,5}$ = 10.2 and $J_{4,3a}$ = 3.6 Hz, H-4), 4.68 (ddd, $J_{3a,6b}$ =11.0, $J_{3a,4}$ = 3.6, and $J_{3a,5}$ = 1.1 Hz, H-3a), 3.88 (br d, $J_{6b,3a}$ =11.0 Hz, H-6b), 2.33 (br d, $J_{6a,5a}$ = 8.3 and $J_{6a,6}$ = 5.4 Hz, H-6a), 2.23 (s, 3H), 2.14 (d, J =1.3 Hz, 3H), 1.94 (br dt, $J_{5a,6a}$ = 8.3 and $J_{5a,6}$ = 4.1, and

$J_{5a,5}$ = 5.0 Hz, H-5a), 0.88 (dd, $J_{6,6a}$ = 5.4 and $J_{6,5a}$ = 4.1 Hz, H-6). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 193.9, 167.3, 128.5, 122.7, 119.8, 116.8, 72.9, 39.1, 29.7, 19.9, 19.7, 15.1, 14.6. IR (KBr, cm^{-1}) 3010, 2213, 1682, 1376, 1216.1, 1092, 1049, 831, 631. Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.85; H, 6.15; N, 6.38.

***rel*-(3a*R*,5a*R*,6*S*,6a*S*,6b*R*)-1-acetyl-2-methyl-5a,6,6a,6b-tetrahydro-3a*H*-cyclopropa[3,4] benzo[1,2-*b*]furan-6-carbonitrile (20):** Colorless liquid, 1.38 g (25%). ^{1}H-NMR (400 MHz, $CDCl_3$)δ 6.09 (dd, $J_{5,4}$ = 10.1 and $J_{5,4}$ = 5.1 Hz, H-5), 5.81 (dd, $J_{4,5}$ =10.1 and $J_{4,3a}$ = 3.7 Hz, H-4), 4.87 (ddd, $J_{3a,6b}$ = 11.4, $J_{3a,4}$ = 3.7, and $J_{3a,5}$ = 0.9 Hz, H-3a), 3.85 (br d, $J_{6b,3a}$ = 11.4 Hz, H-6b), 2.27 (s, 3H), 2.21-2.7 (m, H-6a), 2.17 (d, J =1.3 Hz, 3H), 1.87 (dt, $J_{5a,6a}$ = 8.3 and $J_{5a,6}$ = 5.1 Hz, H-5a), 1.80 (t, $J_{6,6a} = J_{6,5a}$ = 8.3 Hz, H-6). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 193.7, 167.5, 125.1, 124.5, 118.2, 116.2, 74.5, 36.6, 29.7, 17.2, 17.0, 16.0, 13.6. IR (KBr, cm^{-1}) 2930, 2204, 1662, 1340, 1234, 831, 621. Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.63; H, 6.32; N, 6.33.

***rel*-(1*S*,2*S*,5*S*,6*S*,7*R*)-7-cyano-5-(2,4-dioxopentan-3-yl)bicyclo[4.1.0]hept-3-en-2-yl acetate (21):** Colorless liquid, 0.56 g (8%).^{1}H-NMR (400 MHz, $CDCl_3$)δ 5.81 (dd, J =10.1 and 5.5 Hz, 1H), 5.74 (ddd, J = 10.1, 5.5 and 1.5 Hz, 1H), 5.47-5.51 (m, 1H), 3.86 (d, J = 9.3 Hz, 1H), 3.45-3.50 (m, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H), 1.94-1.99 (m, 1H), 1.65-1.70 (m, 1H), 1.58 (t, J = 4.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$)δ 201.7, 201.6, 170.4, 130.4, 123.9, 120.1, 74.1, 63.9, 31.3, 28.9, 28.7, 28.2, 20.8, 19.1, 3.8. IR (KBr, cm^{-1}) (**21** and **22** as a mixture) 3449.1, 2239, 1733, 1701, 1421, 1364, 1237, 1153, 1020, 958, 913.4, 744.7.

***rel*-(1*S*,2*R*,5*S*,6*S*,7*R*)-7-cyano-5-(2,4-dioxopentan-3-yl)bicyclo[4.1.0]hept-3-en-2-yl acetate (22):** Colorless liquid, 0.56 g (8%).^{1}H-NMR (400 MHz, $CDCl_3$)δ 5.58-5.60 (m, 1H), 5.51-5.53 (m, 1H), 5.54-5.58 (m, 1H), 3.64 (d, J = 9.0 Hz, 1H), 3.41 (m, 1H), 2.26 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.21 (m, 1H), 1.72 (ddt, J = 9.4, 5.1, and 1,4. 1H), 1.38 (t, J = 4.7 Hz, 1H). ^{13}C-NMR (100 MHz, CDCl3) δ 201.5, 201.4, 170.1, 126.5, 126.3, 119.7, 72.7, 64.8, 32.8, 30.1, 23.7, 22.1, 21.1, 21.0, 3.6.

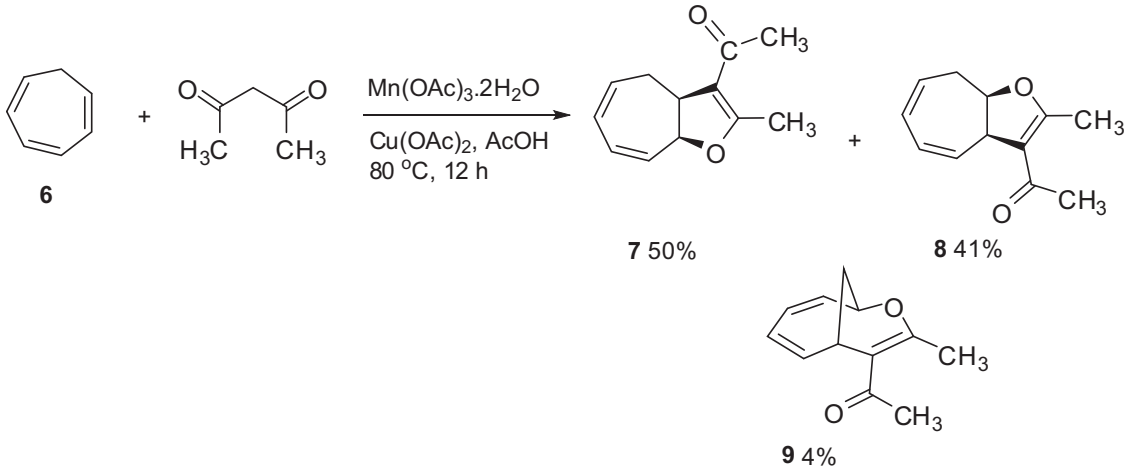
Results and discussion

The reaction of cycloheptatriene **6** with acetylacetone in the presence of excess $Mn(OAc)_3$ (2.7 equiv) and $Cu(OAc)_2$ (0.3 equiv) provided a mixture of products. Chromatography of the mixture on silica gel showed the presence of 3 cycloaddition products, **7**, **8**, and **9,** in yields 50%, 41%, and 4%, respectively (Scheme 3). ^{1}H- and ^{13}C-NMR spectroscopy including 2D-NMR spectral measurements (COSY, HSQC, HMBC) allowed us to identify the correct structures of the products.

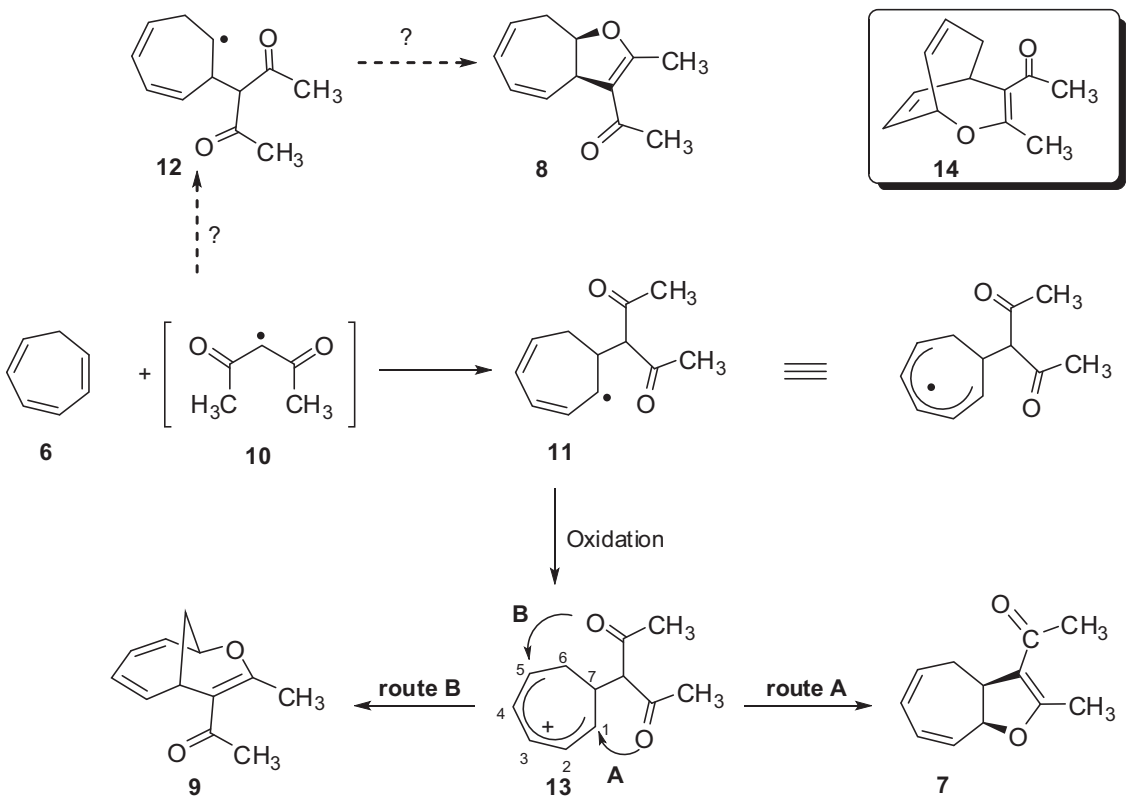
COSY spectra of **7** and **8** showed that the compounds are regioisomers. For the formation of those products we suggest the following mechanism (Scheme 4). The addition of the initially formed radical derived from acetylacetone to the unsymmetrically substituted double bond in **6** can form 2 new radicals: **11** and **12**.

Heiba and Dessau found that $Cu(OAc)_2$ oxidizes secondary radicals 350 times faster than $Mn(OAc)_3$ does and 2 reagents can be used together.[10] Recently, we showed that the initially formed radicals undergo oxidation before the cyclization.[11] The formed carbocation **13**, a pentadienyl cation, is stabilized by delocalization of the positive charge over the ring. The enol form of acetylacetone in **13** undergoes rapid cyclization by the attacks

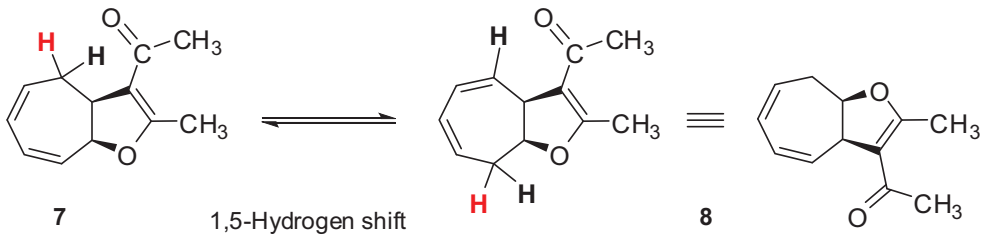
to the carbon atoms C-1 and C-5 to form the products **7** and **9**, respectively. The carbon atom C-4 may also be attacked to form a (4+3) cycloaddition product **14**. However, careful inspection of the reaction mixture did not reveal the formation of any trace of **14**. Geometry optimization of the cation **13** shows that the geometry of the cation does not allow any attack on the carbon atom C-4.



Scheme 3

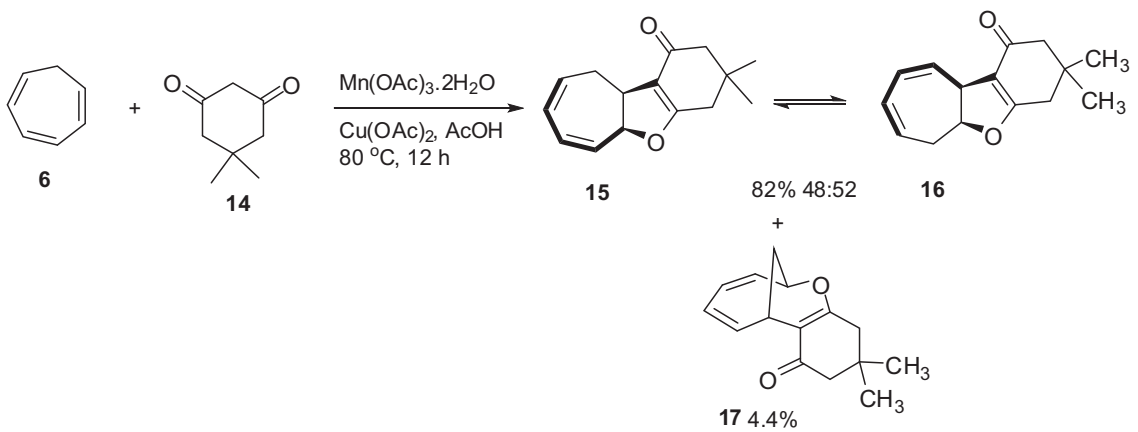


Scheme 4



Scheme 5

The second isomer, **8**, may arise from the oxidation of the formed radical, **12**, followed by a cyclization reaction. The radical **12** is a secondary radical and cannot be stabilized as well as the radical **11**. The formation of **8** in relative high yield (41%) as **7** (50%) raised the question of whether this product is a primary or secondary product. To test this, the isolated regioisomers **7** and **8** were separately heated in AcOH at 80 °C for 12 h (under the reaction conditions). After 12 h, a mixture of **7** and **8** formed in a ratio of 54:46, regardless of the starting isomer (Scheme 5). This ratio was also in agreement with the distribution of yields of **7** and **8**. In conclusion, the isomer **8** is not a primary product and formed under the reaction conditions by thermally allowed 1,5-hydrogen shift from the initially formed isomer **7**. This result shows that acetylacetone exclusively adds to the terminal double bond of cycloheptatriene in a regiospecific manner and forms the most stable carbocation after oxidation.

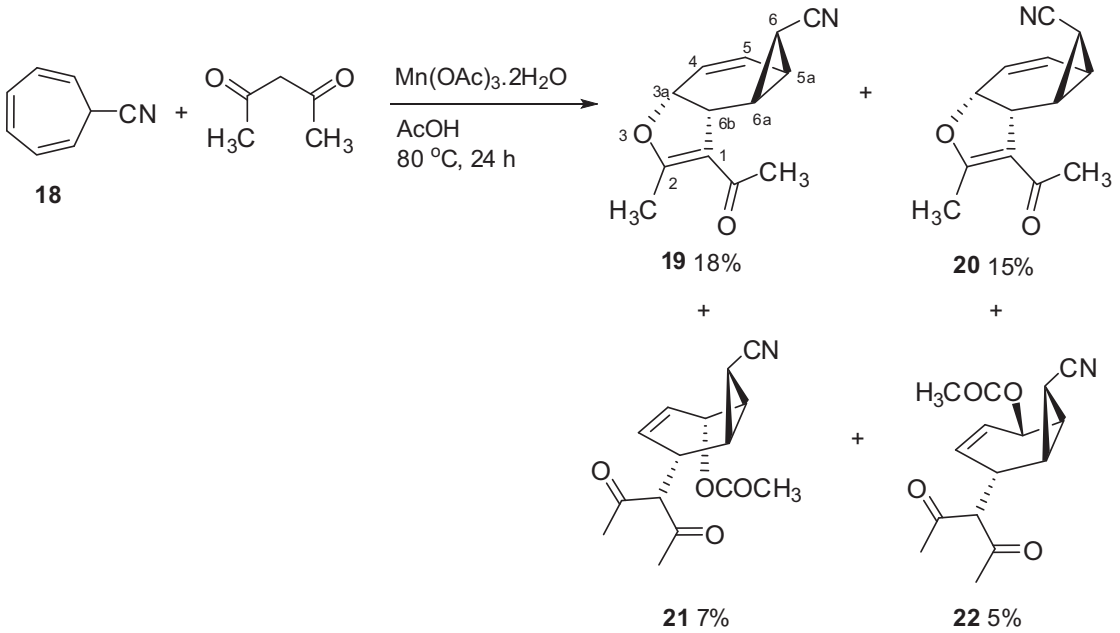


Scheme 6

To gain more insight into the formation mechanism and fate of the above mentioned reaction, dimedone, which has a better enolizable character, was used instead of acetylacetone. The reaction of **6** with dimedone **14** and $Mn(OAc)_3$ in the presence of $Cu(OAc)_2$ gave similar products observed by the reaction of **6** with acetylacetone. The regioisomers **15** and **16** were formed as the main products (82%) in a ratio of 52:48 (Scheme 6). The product **17** was also formed via [6+3] cycloaddition reaction. Furthermore, it has been proved that the regioisomers **15** and **16** are convertible to each other and they form an equilibrium mixture upon heating of the pure isomers.

After the successful synthesis of dihydrofuran-annelated cycloheptadiene derivatives we turned our attention to 7-cyanocycloheptatriene **18**, where the cyano group stabilizes the norcaradiene structure. The starting

material, 7-cyanocycloheptatriene **18,** was synthesized by the reaction of the tropylium cation with cyanide anion as described in the literature.[12]



Scheme 7

The reaction of **18** with acetylacetone in the presence of $Mn(OAc)_3$ in AcOH formed 4 different products of 2 different types. All products were derived from the norcaradiene structure. Fortunately, the major isomers **19** and **20** were separated by chromatography on silica gel. The exact structures of **19** and **20** were assigned from ^{1}H- (COSY, HSQC, HMBC) and ^{13}C-NMR spectra. The most conspicuous features in the ^{1}H-NMR spectrum of these compounds were the 5-membered ring proton resonances. The proton H_{3a} adjacent to the oxygen atom in **19** resonates at δ 4.68 (J = 11.0, 3.6, and 1.1Hz) as a doublet of doublets of doublets. In order to interpret these coupling constants and to determine the exact configuration of the 5-membered ring in **19** and **20** a restricted hybrid HF-DFT SCF calculation on **19** was performed using the basis set 6-31G* as implemented in the Spartan08V111 package program (Figure 1).

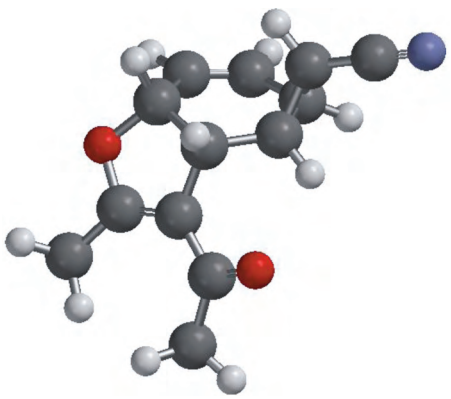
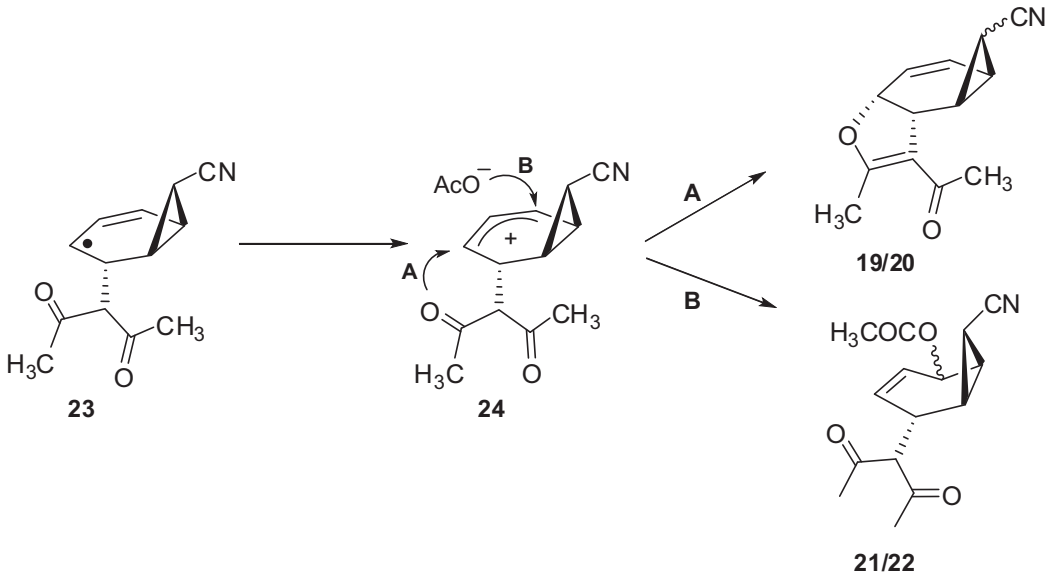


Figure 1. a) Optimized geometry of the most stable conformation of **19**.

The calculations show a dihedral angle of 66.1° for H_{3a}-H_4 in **19**, which is in agreement with the measured coupling constant $J_{3a,4} = 3.6$ Hz. This indicates the *anti*-configuration of the dihydrofuran ring. On the other hand, the observed allylic coupling ($J_{3a,5} = 1.1$ Hz) also shows the *anti*-configuration. A maximum π-contribution to the allylic coupling is observed when ϕ is 90.[13] Our calculation for *anti*-configuration shows that the dihedral angle between the protons H-3a and H-5 is 66.0°, which also is in agreement with the proposed configuration. Furthermore, the small coupling constant between H-6_a and H-6b ($J_{6a,6b} = 1.1$ Hz) also supports the *anti*-configuration. The calculated dihedral angle between those protons is 74° for *anti*-configuration. In the case of a *syn*-configuration of the oxazolidinone ring one would expect a much larger coupling constant due to the calculated smaller dihedral angle (44°). The measured coupling between the oxazolidinone ring protons ($J_{3a,6b} = 11.0$ Hz) shows the *cis*-relation between those protons. The exact configurations of the cyano groups in **19** and **20** were determined by measuring the coupling constants between the cyclopropane protons. The cyclopropyl proton H-6 in **19** resonates as a triplet with a coupling constant of $J = 4.1$ Hz, whereas the *endo*-isomer **20** shows a coupling of 8.3 Hz. Since the *cis*-coupling in cyclopropane is larger than the *trans*-coupling,[13] we assigned the *exo*-configuration to the cyano group in **19**.

It is well established that cycloaddition of cycloheptatriene with singlet oxygen gives adducts derived from cycloheptatriene as well as the norcaradiene structure.[5] In contrast, cycloaddition with dienophiles such as 4-phenyl-triazoline-2,5-dione (PTAD), maleic anhydride, maleimide, or *N*-phenylmaleimide is generally via the norcaradiene tautomer, even in systems that lie towards the cycloheptatriene.[5,14] This can be explained by the planar diene structure of the norcaradiene unit. However, in the light of these observations it is very interesting to note that a cycloheptatriene derivative substituted with an electron withdrawing group, such as a cyano group, also forms norcaradiene-type products upon reaction with $Mn(OAc)_3$ in AcOH. This finding also needs an explanation, since the performed reactions are not Diels-Alder type reactions. A well delocalized diene system is generally more stable than 2 isolated double bonds. On the other hand, a diene system possesses a higher lying HOMO orbital than a double bond. As a consequence of this, a butadiene system is generally more reactive than an isolated double bond.[15] In the case of cycloheptatriene, the conjugation between the double bonds is not well established due to the tube conformation of CHT. Therefore, the double bonds in CHT can be considered as isolated double bonds. On the other hand, the diene unit in norcaradiene forms a planar structure and maximum conjugation. We assume that the initially formed radical derived from acetylacetone adds preferentially to the more reactive C=C double bond of the norcaradiene unit and exclusively from the less-crowded side of the diene unit to form the allylic radical **23**, which undergoes rapid oxidation to form an allylic cation **24**. Furthermore, the formed allylic cation **24** can be stabilized better than in a 7-membered ring. In conclusion, we assume the higher reactivity of the butadiene unit and the formation of a well stabilized allylic cation **24** is the driving force for the exclusive formation of the products derived from the norcaradiene structure.

The formed allylic cation **24** can easily be captured by the oxygen atom of the carbonyl group of acetylacetone to form **19** and **20** (route A) (Scheme 8). Because of the geometrical reason an attack on the other allylic carbon atom (route B) is not possible. However, this carbon atom can be attacked by acetate anion from the *exo*- as well as the *endo*-side of the ring to form **21** and **22**.



Scheme 8

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