Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 63 (2007) 4944–4950
Tetrahedron

Oxidation of some alkoxy-cycloheptatriene derivatives: unusual formation of furan and furanoids from cycloheptatrienes

Ahmet Coşkun,[a,b] Murat Güney,[b] Arif Daştan[b,*] and Metin Balci[c,*]

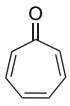
[a]*Selçuk University, Faculty of Education, Department of Chemistry, 42099 Konya, Turkey*
[b]*Atatürk University, Department of Chemistry, 25240 Erzurum, Turkey*
[c]*Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey*

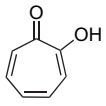
Received 8 January 2007; revised 6 March 2007; accepted 22 March 2007
Available online 27 March 2007

Abstract—The oxidation of some alkoxy tropone and tropone ketal derivatives with singlet oxygen and *m*-chloroperbenzoic acid was investigated. In most cases furan and furanoid derivatives were isolated. The structures of the formed products were determined by means of spectral data and the formation mechanism of these unusual products is discussed.

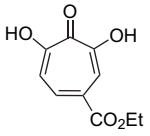
1. Introduction

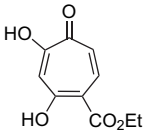
Since their discovery, natural and synthetic tropone (**1**) and tropolone (**2**) derivatives have attracted considerable interest due to the unique structure and properties of the tropolone ring.[1]

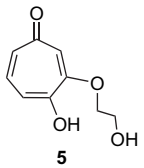

1

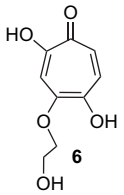

2

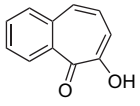
Consequently, over the last 50 years, a large number of ingenious and elaborate approaches for synthesizing this ring system have been developed.[2] The photooxygenation of cyclic 1,3-dienes is one of the most valuable methods for the synthesis of oxygen functionalized target molecules.[3] In connection with the development of new synthetic strategies to tropolones, we recently studied the suitability of bicyclic endoperoxides derived by the cycloaddition of singlet oxygen to the appropriate cyclic dienes and subsequently synthesized isomeric stipitatic acids **3** and **4**,[4] polyoxygenated tropolones **5** and **6**,[5] and some benzotroponoid systems **7** and **8**.[6]

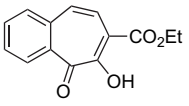

3


4


5


6


7


8

In addition to the synthetic aspects, the chemistry of endoperoxides has fascinated organic chemists for long years.[7] As a direct consequence of this, we have been interested in the oxidation reactions of different tropone and tropolone derivatives in order to develop new synthetic strategies and to furthermore study the chemistry of the formed endoperoxides. We herein describe an expedient route to the formation of some furanoid structures derived from bicyclic endoperoxides.

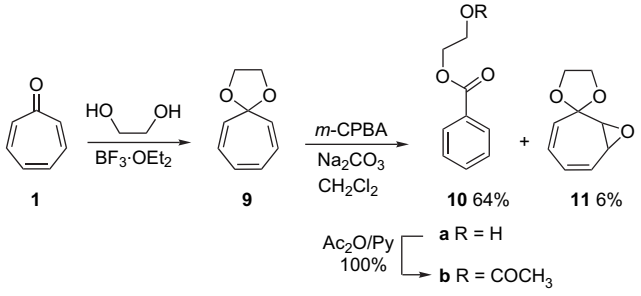
2. Results and discussion

In our first attempted synthesis of tropolone derivatives, we proceeded to subject tropone ketal **9**[8] (that was synthesized from tropone as described in the literature), to an epoxidation reaction.

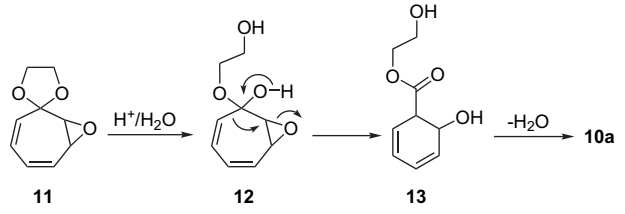
Keywords: Cycloheptatriene; Tropone; Tropolone; Endoperoxide; Singlet oxygen; Rearrangement; Furan derivatives.
* Corresponding authors. Tel.: +90 312 2105140; fax: +90 312 2101280 (M.B.); tel.: +90 442 2314405; fax: +90 442 2360948 (A.D.); e-mail addresses: adastan@atauni.edu.tr; mbalci@metu.edu.tr

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.145

Treatment of ketal **9** with *m*-chloroperbenzoic acid (*m*-CPBA) afforded a mixture, with ethylene glycol monobenzoate **10a**[9] as the major product (Scheme 1). The expected epoxidation product **11** was formed as the minor product. The products were separated by column chromatography on silica gel. For characterization of **10** it was converted to the corresponding acetate **10b**.[10] We assume that the benzoic acid ester **10a** is a secondary product and formed from the rearrangement of the primarily formed epoxide **11**. Opening of the ketal ring in **11** under the reaction conditions may form **12**, which can undergo a pinacol–pinacolone type rearrangement to give **10a** (Scheme 2).



Scheme 1.

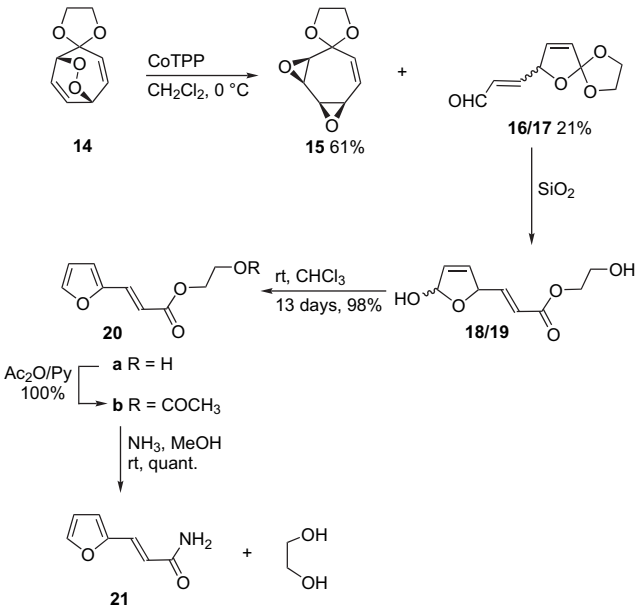


Scheme 2.

Unfortunately, the epoxidation route did not lead to any tropolone derivatives. We therefore turned our attention to the bicyclic endoperoxide **14**[11] synthesized by the addition of singlet oxygen to tropone ketal **9**.

Foote et al.[12] and our group[13] have reported that cobalt-*meso*-tetraphenylporphyrin (CoTPP) promotes the rearrangement of the bicyclic endoperoxides to the corresponding bisepoxide with a *syn*-configuration. In addition to this previously observed reaction of CoTPP, we further demonstrated that some bicyclic endoperoxides derived from cycloheptatriene can be converted into tropolone derivatives upon treatment with CoTPP.[4] For this reason CoTPP-catalyzed decomposition of endoperoxide **14** was investigated. The ^{1}H NMR spectrum of crude mixture showed the formation of bisepoxide **15** and an isomeric mixture of aldehydes **16/17**. After column chromatography, bisepoxide **15** and a mixture of isomeric diols **18/19** were isolated. The initially formed aldehydes **16/17** were rearranged into the rather labile diols **18/19** upon treatment with column material (SiO_2). The diol mixture **18/19** underwent H_2O elimination upon standing at room temperature in $CHCl_3$ and produced the furan derivative **20a**, which was then converted to acetate **20b**, which was confirmed by analysis of the spectral data. Ammonolysis of **20b** gave the known amide **21** (Scheme 3).[14]

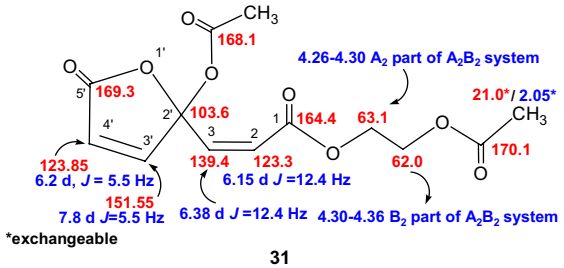
In the light of these observations, we suggest the following mechanism. The initially formed radical **22** resulting from



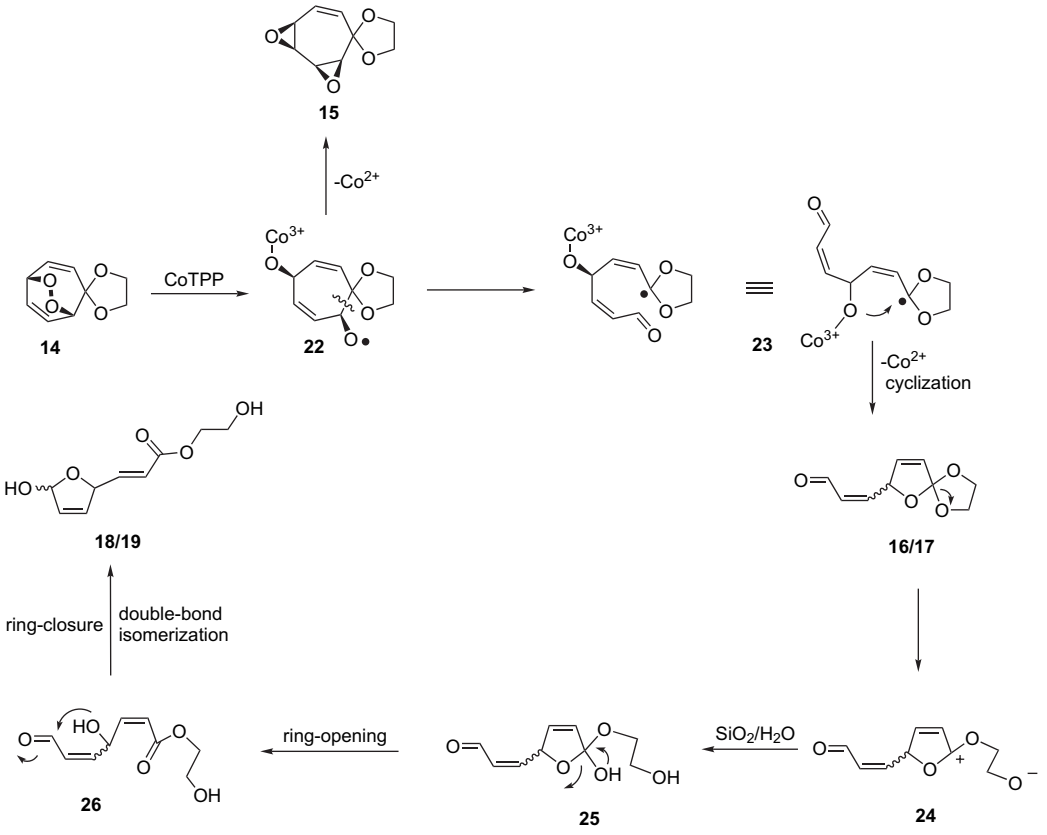
Scheme 3.

the electron transfer reaction between the Co^{2+} species and endoperoxide **14** serves as a key intermediate, as shown in Scheme 4. This intermediate can undergo two different reactions; (i) forming the bisepoxide **15** by the attack of oxygen radicals to the double bond and (ii) cleavage of the carbon–carbon bond in **22** can form the allyl radical **23**, which can then be trapped by oxygen atom to give **16/17**. The formed product has an orthoester structure, which will not be stable and is easily converted to **18/19** via intermediates **24–26**, respectively (Scheme 4).

Next, the tetraphenylporphyrin-sensitized photooxygenation of **27b**,[11] obtained from the NEt_3-catalyzed rearrangement of **14** followed by acetylation, was investigated. The expected singlet oxygen cycloaddition product **28** was converted into **31** under the reaction conditions. Column chromatography of the reaction mixture on silica gel isolated a furanoid **31** in 83% yield. The COSY, HMQC, and HMBC experimental data are in agreement with the proposed structure.

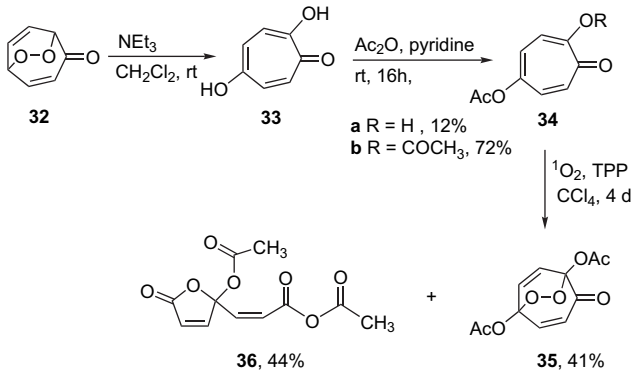


The formation mechanism of the formed furanoid **31** can be rationalized as depicted in Scheme 5. The peroxide linkage in **28** first undergoes a homolytic ring cleavage under the reaction conditions to form the diradical **29**. This cleavage is followed by a C–C cleavage and the formation of the ester carbonyl group. Ring closure takes place between the alkoxy radical and acyl radical in **30** (Scheme 5). We assume that the oxygen functionalities attached to bridgehead carbon atoms in **28** makes the molecule labile.

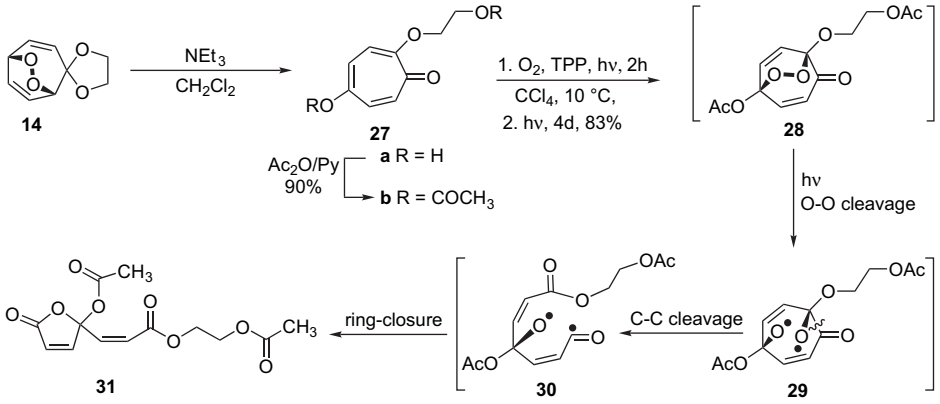


Scheme 4.

In order to test the generality of this interesting transformation of a cycloheptatriene unit into a furanoid structure, we tested the reactivity of the tropolone derivative **34b** with singlet oxygen. The diacetate **34b**[15] was synthesized by the base-catalyzed rearrangement of the tropone endoperoxide **32**[2g,16] followed by acetylation with acetic anhydride in pyridine to give **34a**[17] and **34b**. The diacetate **34b** was then subjected to photooxygenation reaction. NMR spectra of reaction mixture showed the formation of endoperoxide **35** and a rearranged product **36** in 41 and 44%, yields, respectively (Scheme 6). The endoperoxide **35** was isolated by column chromatography in a 4% yield though the rearranged product **36** decomposed. NMR spectral data of **36** was obtained from the NMR spectrum of the crude reaction mixture.

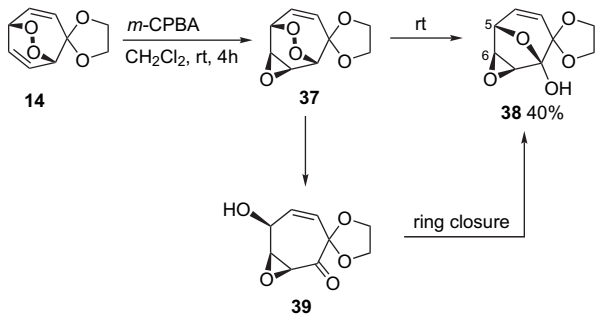


Scheme 6.



Scheme 5.

Finally, we investigated the *m*-chloroperbenzoic acid (*m*-CPBA) oxidation reaction of the cycloheptatriene derivative **14**. The isolated product was identified as the hemiketal **38**. The configuration of the epoxide ring was determined by measuring the coupling constant between the H_5 and H_6 protons. AM1 calculations show that the dihedral angle between those protons is ~65° in the case of *exo*-configuration and ~11° for *endo*-configuration. The dihedral relationship is sufficiently distinctive to be revealed by the magnitude of the spin–spin interaction. Thus, no measurable coupling constant between H_5 and H_6 proton is uniquely accommodated by the *exo*-orientation of the epoxy ring. The formation of **38** can be rationalized by the epoxidation of the sterically less-hindered double bond in **14**, followed rearrangement of the peroxide linkage and intramolecular ring closure (Scheme 7).



Scheme 7.

3. Experimental

3.1. General

Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^1H and ^{13}C NMR spectra were recorded on 400 (100), 200 (50) MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. Methylene chloride was distilled over CaH_2. Pyridine and *n*-hexane were distilled from dry NaOH tablets. Ethyl acetate and carbon tetrachloride was distilled over P_2O_5. Methanol was distilled from magnesium metal activated with iodine. Acetic anhydride was distilled before use at reduced pressure. All substances reported in this paper are in their racemic form.

3.2. Oxidation of 1,4-dioxaspiro[4.6]undeca-6,8,10-triene (9) with *m*-chloroperbenzoic acid (*m*-CPBA)

To a solution of **9** (2.0 g, 13.3 mmol) in methylene chloride (100 mL) were added Na_2CO_3 (5.65 g, 53.3 mmol) and *m*-CPBA (2.30 g, 13.37 mmol). The resulting mixture was stirred for 4 h at room temperature in an ultrasound bath. The precipitate was filtered and dried by evaporating the solvent. The residue was chromatographed on flurosil column (60 g) eluting with *n*-hexane/ethyl acetate (9:1). The first fraction was identified as *m*-chloroperbenzoic acid. The second fraction was monoepoxide **11** isolated as a yellow wax (133 mg, 6%).

*Spiro[1,3-dioxolane-2,2′-[8]oxabicyclo[5.1.0]octa-3,5-diene] (**11**)*: ^1H NMR (200 MHz, $CDCl_3$): 6.03 (m, 3H, H_4, H_5 and H_6), 5.67 (br d, $J_{3,4}$=12.2 Hz, 1H, H_3), 4.13–3.91 (m, 4H, 2×OCH_2), 3.66 (dd, A part of AB system, $J_{1,7}$=4.4, $J_{1,3}$=1.6, 1H, H_1), 3.38 (br d, B part of AB system, $J_{1,7}$=4.4, 1H, H_7). ^{13}C NMR (50 MHz, $CDCl_3$): 132.80, 131.57, 129.81, 129.40, 109.52, 76.61, 67.27, 67.02, 53.18. IR (NaCl film): 3055, 3030, 3004, 2979, 2953, 2902, 1268, 1166, 1140, 1114, 1089, 1013. Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.81; H, 6.14.

The elution of the column was continued with *n*-hexane/ethyl acetate (4:1) and as the third fraction, the benzoic acid ester **10a**[9] was isolated (1.44 g, 64%, as a pale yellow wax).

*2-Hydroxyethyl benzoate (**10a**)*: ^1H NMR (200 MHz, $CDCl_3$): 8.05 (m, 2H, aryl), 7.60–7.39 (m, 3H, aryl), 4.45 (m, A_2 part of A_2B_2 system, 2H, OCH_2), 3.95 (m, B_2 part of A_2B_2 system, 2H, OCH_2), 2.37 (m, 1H, OH). ^{13}C NMR (50 MHz, $CDCl_3$): 168.92, 135.09, 131.95, 131.65, 130.36, 68.62, 63.35. IR (NaCl film): 3438, 3030, 2979, 2953, 2928, 2902, 1702, 1472, 1370, 1319, 1294, 1268, 1114, 706.

3.3. Acetylation of 2-hydroxyethyl benzoate (10a)

To the benzoic acid ester **10a** (100 mg, 0.6 mmol) a solution of acetic anhydride (224 mg, 2.20 mmol) and pyridine (3 mL) was added. The reaction mixture was kept under nitrogen at room temperature for 16 h. The excess acetic anhydride and the solvent were removed under vacuum and the ^1H NMR analysis of residue indicated the formation of the acetate **10b**[10] (pale yellow liquid, 125 mg, 100%).

*2-(Acetyloxy)ethyl benzoate (**10b**)*: ^1H NMR (200 MHz, $CDCl_3$): 8.05 (m, 2H, aryl), 7.60–7.39 (m, 3H, aryl), 4.51 (m, A_2 part of A_2B_2 system, 2H, OCH_2), 4.40 (m, B_2 part of A_2B_2 system, 2H, OCH_2), 2.08 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 172.74, 168.28, 135.09, 131.85, 131.69, 130.38, 64.69, 64.16, 22.75. IR (NaCl film): 3081, 3055, 3030, 2979, 2953, 2927, 1753, 1727, 1447, 1370, 1268, 1243, 1217, 1115, 1064, 1038. MS (EI, 70 eV) *m/z* 208 (M^+, trace), 166 (M^+−acetyl, 1), 136 (2), 106 (100), 77 (26).

3.4. CoTPP-catalyzed reaction of endoperoxide 14

To a magnetically stirred solution of endoperoxide **14** (1.6 g, 8.8 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added cobalt-*meso*-tetraphenylporphyrin (CoTPP) (15 mg, 0.022 mmol) in portions. The mixture was stirred at 0 °C for 20 min. After evaporation of the solvent the residue was chromatographed on silica gel (20 g) eluting with *n*-hexane/ethyl acetate (4:1). The first fraction was identified as bisepoxide **15**[11] (0.98 g, 61%, pale yellow crystals from *n*-hexane/ethyl acetate 1:1 mp 75–76 °C, given as a liquid in the literature[11]).

*Spiro[6,9-dioxatricyclo[6.1.0.0^{5,7}]nona-2-ene-4,2′-[1,3]dioxolane] (**15**)*: ^1H NMR (200 MHz, $CDCl_3$): 5.99 (br dd, A part of AB system, $J_{2,3}$=11.3, $J_{1,2}$=2.4, 1H, H_2), 5.63 (br d, B part of AB system, $J_{2,3}$=11.3, 1H, H_3), 4.10–3.78 (m, 4H, 2×OCH_2), 3.51–3.40 (m, 3H, H_1, H_7, H_8), 3.27 (dd, $J_{5,7}$=4.0, $J_{3,5}$=1.4, 1H, H_5). ^{13}C NMR (50 MHz, $CDCl_3$): 136.29, 128.66, 108.99, 67.43, 66.79, 59.77, 55.84, 54.75, 50.79. IR (KBr film): 3055, 3029, 3004, 2902, 1472, 1446,

1165, 1140, 1114, 1089, 1063, 1012, 987, 936. MS (EI, 70 eV) *m/z* 182 (M^+, 1), 153 (14), 125 (5), 112 (64), 99 (14), 95 (9), 81 (60), 73 (16), 68 (100).

Then the column was eluted with ethylacetate/methanol (95:5) and gave as the second fraction a mixture of isomeric **18** and **19** was isolated (369 mg, 21%, in 3:2 ratio).

*cis and trans 2-Hydroxyethyl (2E)-3-(5-hydroxy-2,5-dihydrofuran-2-yl)prop-2-enoate (**18** and **19**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 6.88 (dd, J=15.6, J=4.8, 1H), 6.75 (dd, J=15.6, J=5.4, 1H), 6.11–5.96 (m, 4H), 5.81 (m, 2H), 5.47 (m, 1H), 5.18 (m, 1H), 5.10 (m, 1H), 5.05 (m, 1H), 4.19–4.11 (m, A_2 parts of A_2B_2 systems, 4H), 3.76–3.68 (m, B_2 parts of A_2B_2 systems, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.91, 166.78, 147.41, 146.53, 132.28, 132.19, 128.83, 128.70, 120.93, 120.70, 103.51, 103.47, 83.99, 83.77, 66.33 (2C), 60.71, 60.33.

3.5. The formation of 20a from 18/19

Compounds **18/19** (40 mg, 0.20 mmol) were dissolved in 0.5 mL of $CDCl_3$ in the NMR tube and its rearrangement was followed by ^{1}H NMR spectroscopy. After 13 days, the compounds **18/19** were completely rearranged to the furan derivative **20a** at room temperature as a brown wax.

*2-Hydroxyethyl (2E)-3-(2-furyl)prop-2-enoate (**20a**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 7.45 (d, $J_{4',5'}$=1.7, 1H, $H_{5'}$), 7.43 (d, A part of AX system, $J_{2,3}$=15.7, 1H, H_3), 6.60 (d, A part of AB system, $J_{3',4'}$=3.2, 1H, $H_{3'}$), 6.45 (dd, B part of AB system, $J_{3',4'}$=3.2, $J_{4',5'}$=1.7, $H_{4'}$), 6.30 (d, X part of AX system, $J_{2,3}$=15.7, 1H, H_2), 4.28 (m, A_2 part of A_2B_2 system, 2H, OCH_2), 3.85 (m, B_2 part of A_2B_2 system, 2H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 167.66, 150.94, 145.19, 131.94, 115.48, 115.29, 112.59, 66.41, 61.39. IR (NaCl film): 3362, 3183, 3080, 3055, 2979, 2953, 2928, 1676, 1625, 1395, 1243, 1217, 783. Anal. Calcd for $C_9H_{10}O_4$: C, 59.34; H, 5.53. Found: C, 59.74; H, 5.38.

3.6. Acetylation of 2-hydroxyethyl (2*E*)-3-(2-furyl)prop-2-enoate (20a)

The reaction was carried out according to the above-mentioned procedure (3.3) by using 100 mg (0.55 mmol) of **20a**, pyridine (3 ml), and acetic anhydride (224 mg, 2.20 mmol). After 16 h, the solvent was evaporated and the ^{1}H NMR analysis of a residue indicated the formation of the acetate **20b** (pale yellow liquid, 111 mg, 90%).

*2-(Acetyloxy)ethyl (2E)-3-(2-furyl)prop-2-enoate (**20b**)*: ^{1}H NMR (200 MHz, $CDCl_3$): 7.49 (m, 1H, $H_{5'}$), 7.44 (d, A part of AX system, $J_{2,3}$=15.8, 1H, H_3), 6.62 (d, A part of AB system, $J_{3',4'}$=3.4, 1H, $H_{3'}$), 6.47 (dd, B part of AB system, $J_{3',4'}$=3.4, $J_{4',5'}$=1.8, 1H, $H_{4'}$), 6.33 (d, X part of AX system, $J_{2,3}$=15.8, 1H, H_2), 4.42–4.29 (m, A_2B_2 system, 4H, 2×OCH_2), 2.09 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 172.70, 168.63, 152.87, 146.83, 133.59, 117.21, 116.91, 114.26, 64.25, 64.17, 22.73. IR (NaCl film): 3055, 3030, 2979, 2953, 1728, 1446, 1395, 1243, 1217, 1185, 1063, 757. Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39. Found: C, 59.05; H, 5.24.

3.7. Ammonolysis of 2-(acetyloxy)ethyl (2*E*)-3-(2-furyl)prop-2-enoate (20b)

The furan derivative (**20b**) (300 mg, 1.34 mmol) was dissolved in 15 mL of absolute methanol. While dry NH_3 was passed through the solution, the mixture was stirred for 2 h at room temperature. After evaporation of methanol and formed acetamide, the ^{1}H NMR spectrum of the crude product showed formation of **21** and ethylene glycol in quantitative yield as a yellow wax (183 mg).

*(2E)-3-(2-Furyl)prop-2-enamide (**21**)*:[14] ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (d, $J_{4',5'}$=2.0, 1H, $H_{5'}$), 7.42 (d, A part of AX system, $J_{2,3}$=15.6, 1H, H_3), 6.60 (d, A part of AX system, $J_{3',4'}$=3.4, 1H, $H_{3'}$), 6.46 (dd, X part of AX system, $J_{3',4'}$=3.4, $J_{4',5'}$=2.0, 1H, $H_{4'}$), 6.30 (d, X part of AX system, $J_{2,3}$=15.6, 1H, H_2). ^{13}C NMR ($CDCl_3$): 167.75, 151.07, 144.97, 131.44, 115.62, 115.07, 112.50.

3.8. Acetylation of 5-hydroxy-2-(2-hydroxyethoxy)-cyclohepta-2,4,6-trien-1-one (27a)

The reaction was carried out according to the above-mentioned procedure (Section 3.3) by using 1.2 g (6.6 mmol) of **27a**,[11] pyridine (30 ml), and acetic anhydride (2.69 g, 26.36 mmol). After 16 h, the excess acetic anhydride and the solvent were removed under vacuum. The product was purified by a short column on silica gel using a mixture of hexane:ethyl acetate (85:15 ratio), yielding 1.58 g (90%) of the diacetate (pale yellow crystals from methylene chloride/*n*-hexane 1:4, mp 85–86 °C).

*4-[2-(Acetyloxy)ethoxy]-5-oxocyclohepta-1,3,6-trien-1-yl acetate (**27b**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 7.11 (d, A part of AB system, $J_{6,7}$=12.8, 1H, H_6), 6.96 (dd, B part of AB system, $J_{6,7}$=12.8, $J_{2,7}$=2.2, 1H, H_7), 6.72 (dd, A part of AB system, $J_{2,3}$=11.0, $J_{2,7}$=2.2, 1H, H_2), 6.67 (br d, B part of AB system, $J_{2,3}$=11.0, 1H, H_6), 4.41 (m, A_2 part of A_2B_2, 2H, OCH_2), 4.20 (m, B_2 part of A_2B_2, OCH_2), 2.22 (s, 3H, CH_3), 2.01 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 179.59, 171.11, 169.54, 163.41, 149.80, 137.15, 133.79, 123.38, 113.05, 67.47, 62.32, 21.13, 21.04. IR (NaCl film): 3055, 3030, 2979, 2953, 2928, 1753, 1574, 1498, 1447, 1370, 1294, 1243, 1217, 1191, 1140, 1114, 936.

3.9. Photooxygenation of 4-[2-(acetyloxy)ethoxy]-5-oxocyclohepta-1,3,6-trien-1-yl acetate (27b)

The diester **27b** (552 mg, 2.07 mmol) and tetraphenylporphyrin (5 mg, 0.008 mmol) were dissolved in 40 mL of CCl_4. The solution was then irradiated with a projection lamp (500 W) while a slow stream of dry oxygen was passed through the solution at 10 °C. After 2 h, the ^{1}H NMR spectral studies indicated the formation of a mixture consisting of **31** and **28** in a ratio of 2:1. The residue was chromatographed on silica gel (20 g) eluting with *n*-hexane/ethyl acetate (7:3). The initially formed endoperoxide **28** was decomposed on the column material. The furanoid **31** (205 mg) was isolated in a yield of 33%. However, when the irradiation was continued with the same projection lamp (500 W) in the absence of oxygen, after 4 days the

endoperoxide **28** was completely converted into the furanoid **31**. A flash chromatography on silica gel allowed to isolate the furanoid **31** in 83% yield as a pale yellow wax, 513 mg.

*2-(Acetyloxy)ethyl(2Z)-3-[2-(acetyloxy)-5-oxo-2,5-dihydrofuran-2-yl]prop-2-enoate (**31**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 7.80 (d, A part of AB system, $J_{3',4'}$=5.5 Hz, 1H, H_3), 6.38 (d, A part of AB system, $J_{2,3}$=12.4 Hz, 1H, H_3), 6.21 (d, B part of AB system, $J_{3',4'}$=5.5 Hz, 1H, $H_{4'}$), 6.15 (d, B part of AB system $J_{2,3}$=12.4 Hz, 1H, H_2), 4.34–4.30 (m, A_2 part of A_2B_2 system OCH_2), 4.29–4.25 (m, B_2 part of A_2B_2 system OCH_2), 2.06 (s, 3H, CH_3), 2.05 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 170.90, 169.32, 168.08, 164.38, 151.55, 139.38, 123.85, 123.28, 103.58, 63.08, 62.01, 21.04, 20.98. IR (NaCl film): 3113, 3061, 2962, 1790, 1733, 1440, 1392, 1373, 1228, 1195, 1079, 1016, 915, 820. MS (EI, 70 eV) *m/z* 195 (M^+−AcOH–CO_2, 2), 168 (4), 153 (4), 137 (6), 125 (5), 109 (5), 88 (100), 83 (20), 71 (10), 54 (24). Anal. Calcd for $C_{13}H_{14}O_8$: C, 52.35; H, 4.73. Found: C, 52.60; H, 5.09.

3.10. Acetylation of 2,5-dihydroxycyclohepta-2,4,6-trien-1-one (33)

The reaction was carried out according to the above-mentioned procedure (Section 3.3) by using 2.0 g (14.5 mmol) of **33**, pyridine (12 ml), and acetic anhydride (5.5 mL). After 16 h, the solvent and excess acetic anhydride were evaporated and ^{1}H NMR analysis of the residue indicated the formation of the diacetate **34b**[15] and monoacetate **34a**.[17] The residue was chromatographed on a silica gel (30 g) column eluting with *n*-hexane/ethyl acetate (95:5). The first fraction was identified as **34a**[17] (321 mg, 12%, brown crystals from methylene chloride/*n*-hexane 1:4, mp 109–110 °C, lit.[17] mp 107–108 °C).

*4-Hydroxy-5-oxocyclohepta-1,3,6-trien-1-yl acetate (**34a**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 8.57 (m, 1H, OH), 7.22 (AA′ part of AA′BB′ system, 2H, H_3, H_6 or H_2, H_7), 7.10 (BB′ part of AA′BB′ system, 2H, H_3, H_6 or H_2, H_7), 2.26 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 172.76, 171.37, 151.29, 133.64, 124.57, 22.84. IR (NaCl film): 3218, 1750, 1563, 1463, 1420, 1268, 1200, 1149, 853, 758. MS (EI, 70 eV) *m/z* 180 (M^+, 3), 168 (6), 139 (100), 131 (9), 111 (63), 91 (38), 75 (30), 65 (17), 55 (22).

The second fraction was identified as **34b**[15] (2.32 g, 72%, brown crystals from methylene chloride/*n*-hexane 1:4, mp 97–98 °C, lit.[15] mp 93–95 °C).

*4-(Acetyloxy)-5-oxocyclohepta-1,3,6-trien-1-yl acetate (**34b**)*: ^{1}H NMR (200 MHz, $CDCl_3$): 7.15 (d, A part of AB system, $J_{2,3}$=$J_{6,7}$=11.7, 2H, H_2, H_7 or H_3, H_6), 6.88 (br d, B part of AB system, $J_{2,3}$=$J_{6,7}$=11.7, 2H, H_2, H_7 or H_3, H_6), 2.32 (s, 3H, CH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 171.00, 168.95, 168.23, 153.66, 131.92, 122.75, 21.12, 20.81. IR (NaCl film): 3048, 1763, 1591, 1370, 1196, 1171, 1143, 1071, 916, 853. MS (EI, 70 eV) *m/z* 222 (M^+, 0.1), 180 (14), 138 (100), 110 (46), 82 (4), 54 (5). Anal. Calcd for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54. Found: C, 59.16; H, 4.64.

3.11. Photooxygenation of 4-(acetyloxy)-5-oxocyclohepta-1,3,6-trien-1-yl acetate (34b)

The reaction was carried out according to the above-mentioned procedure (Section 3.9) by using 2.0 g (9.0 mmol) of **34b** and TPP (10 mg, 0.016) in 200 mL of CCl_4. After 4-day irradiation, the solvent was evaporated and the ^{1}H NMR analysis of residue indicated the formation of the endoperoxide **35** (41%) and furan derivative **36** (44%). The crude mixture was chromatographed on silica gel (20 g) eluting with *n*-hexane/ethyl acetate (5:1). The first fraction was identified as endoperoxide **35** (isolated yield 88 mg, 4%, pale green wax).

*5-(Acetyloxy)-2-oxo-6,7-dioxabicyclo-[3.2.2]nona-3,8-dien-1-yl acetate (**35**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 6.84 (d, $J_{3,4}$=8.4, 1H, H_4), 6.12 (dd, $J_{8,9}$=8.8, $J_{3,9}$=1.8, 1H, H_9), 5.25 (dd, $J_{8,9}$=8.8, $J_{3,8}$=0.7, 1H, H_8), 5.20 (ddd, $J_{3,4}$=8.4, $J_{3,9}$=1.8, $J_{3,8}$=0.7, 1H, H_3), 2.23 (s, 3H, CH_3), 2.22 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 188.32, 168.42, 168.26, 157.68, 146.45, 129.70, 103.25, 83.13, 76.65, 21.00, 20.49. IR (NaCl film): 3093, 2926, 1766, 1706, 1372, 1199, 1171, 1117, 1017, 923, 830. Anal. Calcd for $C_{11}H_{10}O_7$: C, 51.98; H, 3.97. Found: C, 51.24; H, 4.09.

The furan derivative could not be isolated from column, but spectral analyses were performed on the crude products.

*Acetic (2Z)-3-[2-(acetyloxy)-5-oxo-2,5-dihydrofuran-2-yl]-prop-2-enoic anhydride (**36**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 7.70 (d, $J_{3',4'}$=5.5, 1H, $H_{3'}$), 6.31 (d, A part of AB system, $J_{2,3}$=12.5, 1H, H_3), 6.17 (d, $J_{3',4'}$=5.5, 1H, $H_{4'}$), 5.99 (d, B part of AB system, $J_{2,3}$=12.5, 1H, H_2), 2.02 (s, 3H, CH_3), 2.00 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): 169.95, 168.80, 168.73, 151.83, 146.19, 138.98, 124.26, 123.23, 103.71, 20.92, 20.40.

3.12. Oxidation of 14 with *m*-chloroperbenzoic acid

The reaction was carried out according to the above-mentioned procedure (Section 3.2) by using 0.85 g (4.67 mmol) of **14** and *m*-CPBA (0.97 g, 5.60) in 25 mL of CH_2Cl_2. The solvent was removed. The crude was extracted with Et_2O (3×30 mL) and the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified from silica gel (20 g) using *n*-hexane/ethyl acetate 6:4 (white crystals from CH_2Cl_2/*n*-hexane (1:3), 370 mg 40%, mp 138–139 °C).

*Spiro[1-hydroxy-7,9-dioxatricyclo[3.3.1.0^{6,8}]nona-3-ene-2,2′-[1,3]dioxolane] (**38**)*: ^{1}H NMR (400 MHz, $CDCl_3$): 6.29 (dd, A part of AB system, $J_{3,4}$=9.5, $J_{4,5}$=4.0, 1H, H_4), 5.67 (d, B part of AB system, $J_{3,4}$=9.5, 1H, H_3), 4.50 (d, $J_{4,5}$=4.0, 1H, H_5), 4.21–4.04 (m, 4H, OCH_2), 3.96 (m, 1H, OH), 3.73 (d, A part of AB system, $J_{6,8}$=3.1, 1H, H_8), 3.66 (d, B part of AB system, $J_{6,8}$=3.1, 1H, H_6). ^{13}C NMR (50 MHz, $CDCl_3$): 135.11, 132.35, 104.64, 102.53, 74.34, 68.57, 68.15, 59.09, 53.49. IR (NaCl film): 3399, 2983, 2900, 1474, 1373, 1291, 1195, 1167, 1027, 954, 875, 793. MS (EI, 70 eV) *m/z* 198 (M^+, 0.2), 169 (8), 153 (28), 141 (4), 125 (11), 109 (24), 97 (17), 86 (31), 81 (100), 68 (55). Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 53.65; H, 4.84.

Acknowledgements

The authors are indebted to TÜBİTAK (project number 104T401 and TUBİTAK-BAYG National Postdoctoral Fellowship Program for A.C.), Atatürk University, TUBA (Turkish Academy of Sciences) and Middle East Technical University for financial supports. Thanks also to Dr. Cavit Kazaz, Dr. Hamdullah Kılıç, Res. Assistant Barış Anıl, Dr. Ebru Mete for NMR experiments, mass spectra and elemental analyses.

References and notes

1. (a) Banwell, M. G. *Aust. J. Chem.* **1991**, *44*, 1–36; (b) Asao, T.; Oda, M. *Methoden der Organischen Chemie Houben–Weyl*; Regitz, M., Ed.; George Thieme: Stuttgart, 1985; Vol. 5/2c, pp 710–768; (c) Pietra, F. *Acc. Chem. Res.* **1979**, *12*, 132–138; (d) Pietra, F. *Chem. Rev.* **1973**, *73*, 293–364.
2. (a) Scott, A. I.; Lee, E. *J. Chem. Soc., Chem. Commun.* **1972**, 655–656; (b) Scott, A. I.; Weisner, K. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1075–1077; (c) Scott, A. I.; Guilford, H.; Lee, E. *J. Am. Chem. Soc.* **1971**, *93*, 3534–3536; (d) Johns, R. B.; Johnson, A. W.; Murray, J. *J. Chem. Soc.* **1954**, 2352–2356; (e) Bartels-Keith, J. R.; Johnson, A. W.; Taylor, W. I. *J. Chem. Soc.* **1951**, 198–202; (f) Asao, T.; Yahigara, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2131–2135; (g) Oda, M.; Kitahara, M. *Tetrahedron Lett.* **1969**, 3295–3296; (h) Daştan, A.; Yıldız, Y. K.; Kazaz, C.; Balci, M. *Turk. J. Chem.* **2002**, *26*, 143–151; (i) Daştan, A.; Yıldız, Y. K.; Balci, M. *Synth. Commun.* **2001**, *31*, 3807–3815; (j) Shono, T.; Nozoe, T.; Maekava, H.; Kashimura, S. *Tetrahedron Lett.* **1988**, *29*, 555–558; (k) Ikeda, Y.; Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2779–2780; (l) Takeshita, H.; Mori, A.; Suizi, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1429–1432; (m) Güney, M.; Çelik, Z. C.; Daştan, A.; Balci, M. *Can. J. Chem.* **2005**, *83*, 227–235.
3. Balci, M. *Chem. Rev.* **1981**, *81*, 91–108.
4. Dastan, A.; Saracoglu, N.; Balci, M. *Eur. J. Org. Chem.* **2001**, 3519–3522.
5. Dastan, A.; Balci, M. *Tetrahedron* **2006**, *62*, 4003–4010.
6. Güney, M.; Daştan, A.; Balci, M. *Helv. Chim. Acta* **2005**, *88*, 830–838.
7. *Singlet Oxygen*; Wassermann, H. H., Murray, R. W., Eds.; Organic Chemistry, A Series of Monograph; Academic: New York, NY, 1979; Vol. 40.
8. Fukunaga, T.; Simmons, H. E. *J. Am. Chem. Soc.* **1967**, *89*, 5208–5215.
9. (a) Rieche, A.; Schmitz, E.; Beyer, E. *Chem. Ber.* **1958**, *91*, 1935–1941; (b) Wiseman, R. L.; Johnson, S. M.; Kelker, M. S.; Foss, T.; Wilson, I. A.; Kelly, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 5540–5551.
10. Wu, Z.; Stanley, R. R.; Pittman, C. U., Jr. *J. Org. Chem.* **1999**, *64*, 8386–8395.
11. Mori, A.; Takeshita, H. *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku* **1981**, *3*, 125–130.
12. Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641–3642.
13. (a) Sütbeyaz, Y.; Seçen, H.; Balci, M. *J. Org. Chem.* **1988**, *53*, 2312–2317; (b) Balci, M.; Akbulut, N. *Tetrahedron* **1985**, *41*, 1315–1322; (c) Balci, M.; Sütbeyaz, Y. *Tetrahedron Lett.* **1983**, *24*, 311–314; (d) Balci, M.; Sütbeyaz, Y. *Tetrahedron Lett.* **1983**, *24*, 4135–4138.
14. Sanchez, V.; Rebolledo, F.; Gotor, V. *Synlett* **1994**, 529–530.
15. For alternate synthesis of the diacetate, see: Takeshita, H.; Mori, A.; Kusaba, T.; Watanabe, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4325–4333.
16. Secen, H.; Sutbeyaz, Y.; Salamci, E.; Balci, M. *Turk. J. Chem.* **1992**, *16*, 237–245.
17. Kusaba, T.; Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 515–520.