Tetrahedron Vol. 42, No. 23, pp. 6487 to 6494, 1986
Printed in Great Britain.

0040-4020/86 $5.00+.00

PHOTOOXIDATION OF DISPIRO[2.0.2.4]DECA-7,9-DIENE AND ITS ANALOGUES: SYNTHESIS AND PROPERTIES OF NEW NONENOLIZABLE CYCLOHEX-2-ENE-1,4-DIONES

ARMIN DE MEIJERE* and DIETER KAUFMANN

Institut für Organische Chemie, Universität Hamburg,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, West Germany

IHSAN ERDEN*

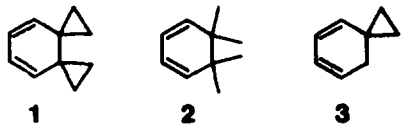
San Francisco State University, Dept. of Chemistry,
1600 Holloway Avenue, San Francisco, CA 94132, USA

(*Received in Germany* 24 *July* 1986)

Abstract : Photooxidation of **1**, **2**, and **3** gave the corresponding 1,4-endoperoxides **4**, **5**, and **6**, respectively, in good yields. Chemical transformations of these provided some new oxygen functionalized cyclohexane and cyclohexene derivatives. The interesting ene-1,4-diones **17** - **19** were prepared by base-catalyzed rearrangement of the endoperoxides and subsequent oxidation of the resulting hydroxyketones **14** - **16** with chromic acid. On the basis of the UV spectra of the diones **17** and **19**, and their comparison with those of other model systems the extent of conjugation with the spirocyclopropane groups in **17** and **19** was established.

INTRODUCTION

Dispiro[2.0.2.4]deca-7,9-diene **1**[1] reacts with most cycloaddends in a normal Diels-Alder mode.[2,3] Its reaction with singlet oxygen ($^1O_2$), a typical 1,4-cycloaddend,[4] should prove a valuable synthetic tool for the preparation of oxygen functionalized derivatives of **1**. Of particular theoretical interest is the 1,4-enedione derived from **1** since a study of its electronic spectrum might provide valuable information on possible conjugative interactions[5] of the spirocyclopropane groups with the 2-ene-1,4-dione moiety. Toward this end we studied the photooxidation of **1**, as well as **2**[6] and **3**[1], which were chosen as suitable model substrates.

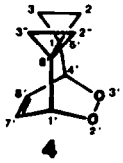


1 **2** **3**

Photooxidation of 1, 2, and 3

Addition of singlet oxygen to **1**, **2**, and **3** was accomplished by irradiating solutions of the dienes in the presence of meso-tetraphenylporphyrin (TPP) while bubbling dry oxygen through the solution. The resulting endoperoxides **4** - **6** were purified by column chromatography at -40°C and identified by spectroscopic methods. By carefully monitoring the progress of the photooxidations by ^{1}H-NMR spectroscopy, it was qualitatively shown that the relative diene reactivities toward $^1O_2$ decrease significantly in the order **3**>**1**>>**2**. The parent 1,3-cyclohexadiene proved to be even more reactive toward $^1O_2$ than **3** under the same conditions. An increase in steric hindrance in the transition state of the cycloaddition

easily accounts for the observed relative reactivities, with one exception: with almost equal coplanar 1,3-diene systems in **1** and **2** (interplanar angle of ~12° and ~18° in **1** and **2**, respectively[1,6]), and comparable van der Waals radii for both the gem-dimethyl and spirocyclopropane groups (actually, the spirocyclopropane appears to be slightly less voluminous than the gem-dimethyl group[7]), the dramatic difference in the diene reactivities of these two compounds cannot be a consequence of steric factors only.



4

5

6

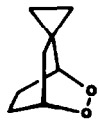
7

Rather, the electronic interaction of the spirocyclopropane groups with the 1,3-diene system in **1**, as the PE-spectrum of **1** clearly indicates,[1] drastically raises its HOMO energy, thus renders it more reactive than the tetramethyl analogue **2**, which lacks a similar conjugative effect.[6] The effect of electron withdrawing substituents in the 5,6-positions of the 1,3-cyclohexadiene on its reactivity toward $^1O_2$ had previously been studied to a limited extent by E. Koch.[8]

The ^{1}H-NMR spectrum of the unsaturated endoperoxide **4** exhibits characteristic signals for the spirocyclopropane groups between 0.15 and 0.67 ppm. The bridgehead protons experience the relatively large deshielding effect of the peroxide bridge (δ = 3.83 ppm), however, they absorb at a significantly higher field ($\Delta\delta$ = 0.83 ppm) than their counterparts (δ = 4.66 ppm) in the parent 2,3-dioxabicyclo[2.2.2]oct-2-ene **7**,[9] obviously due to the diamagnetic anisotropy of the adjacent spirocyclopropane groups. Accordingly, one observes two signals at 3.56 and 4.63 ppm for the two bridgehead protons in the ^{1}H-NMR spectrum of **6**. The corresponding protons in **5** absorb at 3.81 ppm, 0.85 ppm higher than in **7**, presumably due to the electron releasing inductive effect of the gem-dimethyl groups.

Various chemical transformations, with emphasis on those of **4**, furnished definitive proof for the structures of the endoperoxides **4** - **6**. Selective reduction of the endocyclic double bonds in **4** and **6** with diazene[10] gave the corresponding saturated endoperoxides **8** and **9** in high yields. Thermolysis of **4** in CCl_4 solution at 120°C in a sealed tube gave rise to a mixture of the endo-diepoxide **10** and the epoxyketone **11** in a ratio of 40:60. Under photochemical conditions (366 nm, n-pentane), a 30:70 mixture of **10** and **11** was obtained. Attempted chromatography on silica gel at room

8



9

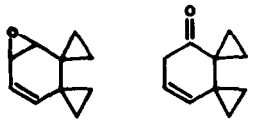
10

11

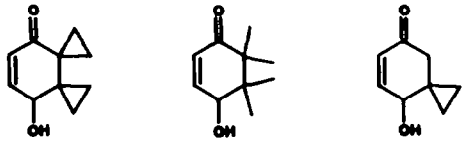
temperature resulted in the isolation of the hydroxyenone **14** (vide infra) as the sole product. Separation of the isomers **10** and **11** was achieved by fractional sublimation. Only the diepoxide **10** sublimed at 0.01 mm and 40°C readily, leaving **11** as pot residue behind. The ratio of the diepoxide to epoxyketone drastically improved in favor of **10** when endoperoxide **4** was allowed to react with a catalytic amount of cobalt tetraphenylporphyrin (CoTPP)[11] at room temperature. Under

these conditions an 80:20 mixture of **10** and **11** was formed. The fact that **10** was accompanied by the epoxyketone in the CoTPP-catalyzed isomerization of **4** is somewhat surprising, since the corresponding reactions of several other endoperoxides had been reported to yield diepoxides exclusively.[12]

Treatment of **4** with triphenylphosphine followed by flash distillation of the product gave an 85:15 mixture of **12** and **13**. The formation of **13** presumably resulted from partial isomerization of **12** during the distillation (pot temp. 40°C). However, the corresponding isomerizations in similar systems do not take place as readily, and can only be affected at ambient temperatures by Pd(0)-catalysts.[13]



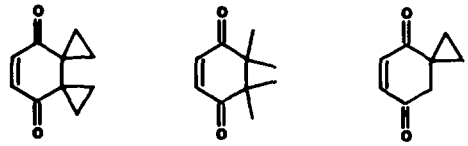
12 **13**



14 **15** **16**

For the synthesis of the desired enediones, the Kornblum-de la Mare type base-catalyzed isomerization of endoperoxides was exploited.[14] Treatment of the endoperoxides **4** - **6** with catalytic amounts of triethylamine (KOH gave better results in the case of **5**) smoothly converted them into the corresponding hydroxyenones **14** - **16**. The exclusive formation of **16** from **6** is remarkable and deserves some comment. In unsymmetrically substituted endoperoxides two major factors ought to dictate the chemoselectivity in the base-catalyzed rearrangement: the relative acidities of the bridgehead protons and the steric requirement of the transition state of the base attack on either of these protons. The former factor would not account for the observed isomer **16** since the cyclopropyl group in a perpendicular arrangement is known to exert an electron-withdrawing effect on a neighboring atom,[15] and should thus acidify the adjacent bridgehead position in **6**. Therefore, the steric factor must be outweighing the acidity factor in the present case. The base attack on **6** proceeds here from the sterically least hindered side leading to **16** as the sole product.

The hydroxyenones **14** - **16** were characterized by spectroscopic methods and used in the next step without further purification. Their oxidation to the 1,4-diones was accomplished in excellent yields with chromic acid in a two phase system. Other oxidation methods, however, employing activated MnO_2 or pyridiniumchlorochromate (PCC) have also been successfully applied to similar systems,[16] and would have worked equally well here. The enedi-

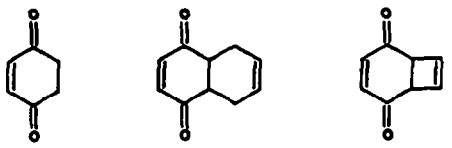


17 **18** **19**

ones **17** - **19** thus obtained, were purified by column chromatography for analytical and spectroscopic characterization. The most characteristic signal in the ^{1}H-NMR spectra of these non-enolizable enediones is the sharp singlet at ~6.8 ppm. Moreover, the cyclopropyl hydrogens which are exposed to the paramagnetic anisotropy cone of the adjacent carbonyl group in **17** and **19** are significantly shifted downfield (1.28 and 1.42, respectively) in the NMR spectrum.

Discussion of the spectroscopic characteristics of **17** - **19**

The UV data and IR carbonyl stretch frequencies of the cyclohex-2-ene-1,4-diones **17** - **19** are listed in table 1 along with those of compounds **20**[17], **21**[18,19] and **22**[18] with similar structural features.



20 **21** **22**

Table 1. UV and IR-Data of **17** - **19** and Reference Compounds **20** - **22**

Compd.	UV (EtOH) λ_{max} [nm]	ε_{max}	IR (KBr) νC=O [cm^{-1}]
17	224	13300	1670
	275	300	
	335	110	
	380 sh	19	
18	224	6000	1682
	332	18	
19	206	4000	1675
	292	320	1685[a]
	330 sh	150	
20[17]	233	15100	1690
	352	64	
21[18]	223	11900	1681[19]
	360	60	
22[18]	222	11800	1675
	365	97	

[a] Film

The conjugative effect in any such compound becomes most evident in the position and extinction coefficient of its UV absorption maximum due to the $n \rightarrow \pi^*$ transition, which normally is the longest wavelength band. The corresponding maxima for **17**, **18**, and **19** are at 335, 332, and 330 nm respectively, with virtually the same position for all three diones, but with a striking difference in the extinction coefficients of 110, 18, and 147, respectively. The UV spectrum of the dispirodecenedione **17** also exhibits a rather flat shoulder at approximately 380 nm reaching out to 400 nm, which must be responsible for the slightly yellow appearance of crystalline **17**. It is uncertain whether this feature resembles a similarity of **17** with p-benzoquinone, which shows an absorption band at 434 nm.[20] It is apparent, however, that the UV spectra of both spiro compounds **17** and **19** differ distinctly from those of the cyclohexenediones **20**, **21**, and **22** (see table 1).

EXPERIMENTAL PART

General remarks. Melting points (uncorrected) were determined with a melting point apparatus by Wagner & Munz, Munich. - UV: Perkin-Elmer-Hitachi 200. - IR: Perkin Elmer 297, 399. - MS: Varian MAT 311 and 311 A. - ^{1}H-NMR: Bruker WH 270, Varian EM 360; δ = 0 for tetramethylsilane, δ = 7.26 for chloroform. - ^{13}C-NMR: Varian CFT 20, Bruker WH 270 (67.88 MHz), Bruker WM 400 (110.62 MHz); δ = 0 for tetramethylsilane, δ = 77.0 for chloroform. - Elemental analyses were performed in-house in the microanalytical laboratory, University of Hamburg.

General procedure for the preparation of endoperoxides **4**, **5**, and **6**: A solution of 1.0 g of the diene and 2-3 mg of meso-tetraphenylphorphyrin in 80 ml of CCl_4 was placed in a 200 ml pear shaped flask. While cooling in an ice-water bath and bubbling dry oxygen through the solution the reaction flask was irradiated with a 250 W high pressure sodium vapor lamp. The progress of singlet oxygen addition was monitored by TLC and ^{1}H-NMR.

After completion of the reaction the solvent was removed by rotoevaporation (0°C, 20 Torr) and the crude product purified by low temperature chromatography on silica gel (CH_2Cl_2/n-pentane = 2:1).

Dispiro[cyclopropane-1,5'-[2,3]dioxabicyclo[2.2.2]oct-7-ene-6',1"-cyclopropane] (**4**), 956 mg (77%), m.p. 109 - 110°C. - IR (KBr): 3078, 3005, 2960, 1640, 1436, 1360, 1280, 1050, 1030 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.15 (m, 3(3")-H_{endo}), 0.42 (m, 2(2")-H_{endo}, 3(3")-H_{exo}), 0.67 (m, 2(2")-H_{exo}) 3.83 (m, 1'(4')-H), 6.76 (m, 7'(8')-H). - ^{13}C-NMR (67.88 MHz, $CDCl_3$, δ, ppm): 6.86, 8.73, 23.03, 80.29, 131.9. - (Found: C, 73.29; H, 7.33. Calc. for $C_{10}H_{12}O_2$ (164.21): C, 73.15; H, 7.37).

7,7,8,8-Tetramethyl-2,3-dioxabicyclo-[2.2.2]oct-5-ene (**5**), 840 mg (68%), m.p. 106 - 108°C. - IR (KBr): 2980, 1640, 1046, 1030 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.76 (s, 2 CH_3), 1.15 (s, 2 CH_3), 3.81 (m, 1(4)-H), 6.56 (m, 5(6)-H). - (Found 168.11463. Calc. for $C_{10}H_{16}O_2$, 168.11502).

Spiro[cyclopropane-1,5'-[2,3]dioxabicyclo[2.2.2]oct-7-ene] (**6**), 780 mg (60%), IR (film): 3070, 3038, 2930, 2880, 1606, 1500, 1408, 1030, 905 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.18 (m, 3-H_{endo}), 0.46 (m, 3-H_{exo}), 0.65 (m, 2-H_2), 1.49 (dd, ^2J = 13.2, ^3J = 2.0 Hz, 6-H_{exo}), 2.12 (dd, ^2J = 13.2, ^3J = 4.0 Hz, 6-H_{endo}), 3.56 (m, 1'-H), 4.63 (m, 4'-H), 6.58 (m, 5(6)-H). - (Found 138.06820. Calc. for $C_8H_{10}O_2$, 138.06807).

General procedure for the diazene reduction of **4** and **6**: Endoperoxide (1.45 mmol) was dissolved in 25 ml of dry CH_2Cl_2, 4.35 g of freshly prepared potassium azodicarboxylate was added, the resulting slurry was placed in an ice-water bath. A solution of 2.05 g of glacial acetic acid in 5 ml CH_2Cl_2 was added dropwise with stirring, and the mixture stirred at 0 - 15°C for 3 h. The salt was filtered off by suction, the mother liquour washed with 100 ml of water, the organic layer dried over Na_2SO_4 and was then rotoevaporated (0°C, 20 Torr). The saturated endoperoxide was then purified by low temperature column chromatography on silica gel at -40°C (CH_2Cl_2/n-pentane = 3:1).

Dispiro[cyclopropane-1,5'-[2,3]dioxabicyclo[2.2.2]octane-6',1"-cyclopropane] (**8**), 205 mg (85%), m.p. 70 - 71°C. - IR (KBr): 3078, 3005, 2940, 1456, 1440, 1250, 1218, 1075, 1062, 997, 950, 935 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.10 - 0.90 (m, 2(2", 3,3")-H_2), 2.10 (m, 7'(8')-H), 3.30 (m, 1'(4')-H). - (Found: C, 73.10; H, 8.48. Calc. for $C_{10}H_{14}O_2$ (166.22): C, 72.26; H, 8.49).

Spiro[cyclopropane-1,5'-[2,3]dioxabicyclo[2.2.2]octane] (**9**), 167 mg (82%), IR (film): 3080, 3005, 2980, 2940, 1455, 1440, 1310, 1028, 996, 950, 935 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.47 (m, 3-H_2), 0.56 (m, 2-H_{endo}), 0.79 (m, 2-H_{exo}), 1.68 - 2.31 (m, 6'(7',8')-H_2), 3.15 (m, 4'-H), 4.22 (m, 1'-H).

Thermal rearrangement of **4** to **10** and **11**: A solution of 200 mg of the endoperoxide in 2 ml of CCl_4 was placed in a thick-walled test tube which was then sealed under nitrogen and heated at 120°C for 4 h. After cooling to room temperature, the solvent was rotoevaporated. Attempts to separate the isomers by column chromatography on silica gel failed, however, the product mixture was separated by fractional sublimation at 0.01 Torr and 40°C. Under these conditions the diepoxide **10** deposited on the cold-finger as a white solid. The pot residue consisted almost exclusively of the epoxyketone **11** containing

traces of **10**.

endo-7,8,9,10-Bisepoxydispiro[2.0.-2.4]decane (**10**), 69 mg (34%), m.p. 112 - 113°C. - IR (KBr): 3080, 3010, 2920, 930, 910 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.35 (m, 1(2,5,6)-H_{endo}), 0.44 (m, 2(6)-H_{exo}), 0.70 (m, 1(5)-H_{exo}), 2.64 (m, 7(10)-H), 3.49 (m, 8(9)-H). - ^{13}C-NMR (100.62 MHz, $CDCl_3$, δ, ppm): 8.09, 8.18,, 17.98, 48.91, 56.74. - (Found: C, 73.10; H, 7.40. Calc. for $C_{10}H_{12}O_2$ (164.2): C, 73.15; H, 7.37).

9,10-Epoxydispiro[2.0.2.4]decan-7-one (**11**), 103 mg (52%), m.p. 70 - 71°C. - IR (KBr): 3010, 2980, 2910, 1695, 1315 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.23 (m, 2H), 0.60 (m, 3H), 0.78 (m, 1H), 1.06 (m, 1H), 1.20 (m, 1H), 2.76 (d, ^3J = 4.2 Hz, 1H), 2.88 (dd, ^2J = 18.8, ^3J = 1.4 Hz, 1H, A-part of an ABX-system), 3.09 (ddd, ^2J = 18.8, ^3J = 2.8, 0.8 Hz, 1H, B-part), 3.43 (m, 1H).

Photolysis of **4**: A solution of 200 mg **4** in 150 ml dry n-pentane was irradiated with a 125 W medium pressure mercury vapor lamp (Hanau) through a pyrex filter for 1 h, while bubbling a slow stream of dry nitrogen through the solution. The solvent was removed by rotoevaporation (20 Torr, 20°C) to give 156 mg (78%) of a mixture of **10** and **11** (ratio 30:70, by ^{1}H-NMR).

Cobalt tetraphenylporphyrin catalyzed isomerization of **4**: To a solution of 150 mg of **4** in dry CH_2Cl_2, 10 mg of CoTPP was added and the mixture stirred at room temperature for 1 h. After rotoevaporation of the solvent, the residue was sublimed at 0.01 Torr and 70°C to give 130 mg (86%) of a 4:1 mixture of **10** and **11**.

Reaction of **4** with triphenylphosphine: A solution of 200 mg (1.22 mmol) of **4** in 5 ml of CH_2Cl_2 was placed in a 10 ml single neck round-bottomed flask equipped with a magnetic spin-bar. The flask was immersed in an ice-water bath, and solid triphenylphosphine (0.32 g, 1.22 mmol) was slowly added. The mixture was stirred at room temperature for 2 h, the solvent removed by rotoevaporation (20 Torr, 0°C) and the residue flash distilled (0.01 Torr, 40°C) to give 156 mg (87%) of a colorless liquid which, according to its ^{1}H-NMR spectrum, consisted of a 87:13 mixture of **12** and **13**.

9,10-Epoxydispiro[2.0.2.4]dec-7-ene (**12**): IR (film): 3076, 3005, 1632, 1428, 1050, 1020, 970 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.15 (m, 1H), 0.25 (m, 1H), 0.34 (m, 1H), 0.44 - 0.69 (m, 4H), 0.74 (m, 1H), 2.83 (d, ^3J = 4.3 Hz, 10-H), 3.36 (ddd, ^3J = 4.3, 4.2, ^4J = 1.6 Hz, 9-H), 5.35 (dd, ^3J = 9.7, ^4J = 1.6 Hz, 7-H), 5.98 (dd, ^3J = 9.7, 4.2 Hz, 8-H).

Dispiro[2.0.2.4]dec-9-en-7-one (**13**): IR (film, in the mixture **12** + **13**): 1695 (νC=O). - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.44 - 0.69 (m, 6H), 1.14 (m, 2H), 3.06 (dd, ^3J = 3.6, ^4J = 1.8 Hz, 8-H_2), 5.48 (dt, ^3J = 10.0, ^4J = 1.8 Hz, 10-H), 5.75 (dt, ^3J = 10.0, 3.6 Hz, 9-H).

Synthesis of **14** and **16** by triethylamine catalyzed isomerization of **4** and **6**: To a solution of 200 mg of endoperoxide in 5 ml of dry CH_2Cl_2 50 mg of freshly distilled triethylamine was added, and the mixture was stirred at room temperature for 3 h. The solvent was removed at reduced pressure (20 Torr and 20°C) and the residue purified by column chromatography on silica gel (CH_2Cl_2/diethyl ether = 1:3).

10-Hydroxydispiro[2.0.2.4]dec-8-en-7-one (**14**), 160 mg (80%), IR (film): 3680, 3600, 3460, 3160, 3082, 3040, 3010, 2925, 2858, 1670, 1380,

1315 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.19 (m, 2H), 0.43 - 0.69 (m, 4H), 0.98 (m, 1H), 1.15 (m, 1H), 3.07 (br. s, exchanges with D_2O, O-H), 4.04 (m, 10-H), 6.03 (d, ^3J = 10.0 Hz, 8-H), 6.96 (dd, ^3J = 10.0, 3.8 Hz, 9-H).

8-Hydroxyspiro[2.5]oct-6-en-5-one (**16**), 130 mg (90%), IR (film): 3420, 3080, 3040, 3010, 1680, 1415, 1380, 1265, 1168, 1030 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.43 (br. s, 2H), 0.61 (m, 1H), 0.76 (m, 1H), 2.16 (d, ^2J = 16.8 Hz, 1H, A-part of an AB-system), 2.56 (br. s, exchanges with D_2O, O-H), 2.59 (d, ^2J = 16.8 Hz, 1H, B-part), 3.98 (m, 8-H), 6.03 (d, ^3J = 10.0 Hz, 6-H), 6.94 (dd, ^3J = 10.0, 4.0 Hz, 7-H).

Synthesis of **15** from **5** with KOH: To a stirred, ice-cooled solution of 70 mg of **5** in 5 ml of methanol a solution of 100 mg KOH in 5 ml of methanol was added dropwise. The mixture was stirred for 4 h at 0°C, then neutralized with glacial acetic acid and the solvent removed by rotoevaporation. Water (50 ml) was added to the residue and the mixture extracted with CH_2Cl_2 (4x 10 ml). The combined CH_2Cl_2 extracts were dried over Na_2SO_4 and the solvent rotoevaporated. The product was purified by chromatography on a short silica gel column (CH_2Cl_2/diethyl ether = 1:3) to give 4-hydroxy-5,5,6,6-tetramethylcyclohex-2-en-1-one (**15**), 66 mg (94%), IR (film): 3460, 2980, 1680, 1470, 1380, 1370, 1052 cm^{-1}. - ^{1}H-NMR (60 MHz, $CDCl_3$, δ, ppm): 0.85 (s, CH_3), 1.10 (s, 3 CH_3), 2.50 (br. s, exchanges with D_2O, O-H), 4.45 (dd, ^3J = 3.0, ^4J = 2.0 Hz, 4-H), 5.95 (dd, ^3J = 10.0, ^4J = 3.0 Hz, 2-H), 6.75 (dd, ^3J = 10.0, 2.0 Hz, 3-H).

Synthesis of **17**, **18**, and **19**. General procedure for the oxidation of **14** - **16**: In a 50 ml round-bottom, two-necked flask equipped with a magnetic spin-bar, an immersing thermometer and a dropping funnel, was placed 9.15 mmol of hydroxy-enone, and the flask was cooled to -5°C by means of an ice-salt bath. To this, 5 ml of water was added, followed by dropwise addition of a cold solution of 1.15 g of CrO_3 in 1.8 ml of conc. H_2SO_4 and 5 ml of H_2O at a rate as to maintain the temperature of the reaction mixture at or below 0°C. After complete addition, the mixture was stirred at -5 to 0°C for 1 h, 15 ml of CH_2Cl_2 was then added, and the two layers separated. The aqueous layer was extracted twice with 25 ml each of CH_2Cl_2, the combined organic layers were dried over Na_2SO_4, and the solvent rotoevaporated. The product was purified by chromatography on a silica gel column, eluting with CH_2Cl_2.

Dispiro[2.0.2.4]dec-8-en-7,10-dione (**17**), 128 mg (85%), m.p. 62 - 63°C. - IR (KBr): 3080, 3040, 3010, 2930, 1670, 1603, 1425, 1413, 1380, 1305, 1085 cm^{-1}. - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.65 (4-line m, 1(2,5,6)-H_{endo}), 1.28 (4-line m, 1(2,5,6)-H_{exo}), 6.89 (s 8(9)-H). - ^{13}C-NMR (67.88 MHz, $CDCl_3$, δ, ppm): 15.6, 31.2, 151.1, 197.7. - UV (EtOH, λ_{max}, nm): 224 (ε = 13300), 275 (ε = 300), 335 (ε = 110), 380 sh (ε = 19). - (Found: C, 74.12; H, 6.22. Calc. for $C_{10}H_{10}O_2$ (162.19): C, 74.06; H, 6.22).

5,5,6,6-Tetramethylcyclohex-2-en-1,4-dione (**18**), 129 mg (84%), m.p. 126 - 126.5°C. - IR (KBr): 3045, 2985, 2930, 1682, 1605, 1468, 1318, 1080 cm^{-1}. - ^{1}H-NMR (60 MHz, $CDCl_3$, δ, ppm): 1.10 (s, 4 CH_3), 6.84 (s, 2(3)-H). - UV (EtOH, λ_{max}, nm): 224 (ε = 6000), 332 (ε = 18). - (Found: C, 72.31; H, 8.50. Calc. for $C_{10}H_{14}O_2$ (166.22): C, 72.26; h, 8.49).

Spiro[2.5]oct-5-en-4,7-dione (**19**), 113 mg (90%), IR (film): 3010, 1675, 1606, 1413, 1378, 1350, 1279, 1090 cm^{-1}. - ^{1}H-NMR (60 MHz, $CDCl_3$, δ,

ppm): 0.84 (m, 1(2)-H_{endo}), 1.42 (m, 1(2)-H_{exo}), 2.80 (s, 8-H), 6.80 (s, 6(7)-H). - UV (EtOH, λ_{max}, nm): 206 (ε = 4000), 292 (ε = 320), 330 sh (ε = 150). - (Found: C, 70.48; H, 5.96. Calc. for $C_8H_8O_2$ (136.15): C, 70.58; H, 5.92).

ACKNOWLEDGEMENTS

Financial support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, a NATO research grant, and a DAAD (German Academic Exchange Service) Study Visit grant is gratefully acknowledged.

REFERENCES AND NOTES

1 A. de Meijere, Chem. Ber. **107**, 1684 (1974).

2 A. de Meijere, Chem. Ber. **107**, 1702 (1974).

3 Tetracyanoethylene (TCNE) is an exception in that it preferentially attacks the bicyclopropyl moiety rather than the 1,3-diene system in **1**: D. Kaufmann, A. de Meijere, B. Hingerty, and W. Saenger, Angew. Chem. **87**, 842 (1975); Angew. Chem. Int. Ed. Engl. **14**, 816 (1975); B. König, D. Kaufmann, R. Näder, and A. de Meijere, J. C. S. Chem. Commun. **1983**, 771.

4 H.H. Wasserman and R.W. Murray, Singlet Oxygen, Academic Press, New York (1979).

5 For a recent review see: A. de Meijere, Angew. Chem. **91**, 867 (1979); Angew. Chem. Int. Ed. Engl. **18**, 809 (1979).

6 D. Kaufmann and A. de Meijere, Chem. Ber. **116**, 1897 (1983).

7 Cf. ref. 6 and: K. Alder, H.-J. Ache, and F.H. Flock, Chem. Ber. **93**, 1888 (1960).

8 E. Koch, Tetrahedron **24**, 6295 (1968), and references cited therein.

9 G.O. Schenk and W. Willmund, reported by R. Criegee in Houben-Weyl, "Methoden der Organischen Chemie", Vol. VIII, E. Müller Ed., 4th. ed., Thieme, Stuttgart 1952, p. 16.

10 R.G. Salomon and M.F. Salomon, J. Am. Chem. Soc. **99**, 3501 (1977).

11 C.H. Foster and G.A. Berchtold, J. Am. Chem. Soc. **94**, 7939 (1972); K.H. Maheshwari, P. de Mayo, and D. Wiegand, Can. J. Chem. **48**, 3265 (1970).

12 Cf. J.D. Boyd, C.S. Foote, and D.K. Imagawa, J. Am. Chem. Soc. **102**, 3641 (1980).

13 M. Suzuki, Y. Oda, and R. Noyori, J. Am. Chem. Soc. **101**, 1623 (1979).

14 M. Kornblum and H.E. de la Mare, J. Am. Chem. Soc. **73**, 880 (1951).

15 Cf. B.R. Ree and J.C. Martin, J. Am. Chem. Soc. **92**, 1660 (1972); V. Buss and P. von R. Schleyer, ibid. **93**, 3927 (1971); D.S. Kabakoft and E. Namanworth, ibid. **92**, 3234 (1970).

16 I. Erden, Synth. Commun. **14**, 989 (1984).

17 E.W. Garbisch, Jr., J. Am. Chem. Soc. **87**, 4971 (1965).

18 M. Oda, Y. Kayama, and Y. Kitahara, Tetrahedron Lett. **1974**, 2019.

19 J.A. Baltrop and M.L. Burstall, J. Chem. Soc. **1959**, 2183.

20 E.A. Braude, J. Chem. Soc. **1945**, 1490.