# 106. Photochemical Reactions

128th Communication[1])

# Isolation of a Thermally Labile 2,8-Dioxabicyclo[3.2.1]oct-3-ene Intermediate on Photolysis of 3,4:5,6-Diepoxy-5,6-dihydro-β-ionone

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*Summary*

Photolysis ($\lambda = 254$ mm, THF) of the diepoxyenone (*E*)-**1** at −78° leads to the 2,8-dioxabicyclo[3.2.1]oct-3-ene intermediate **3** (51%). At ambient temperature **3** undergoes an unexpectedly rapid electrocyclic opening to the triketone **2** in quantitative yield. Compound **3** seems likely to be the intermediate in the acid-catalyzed rearrangement of (*E*)-**1** → **18** also.

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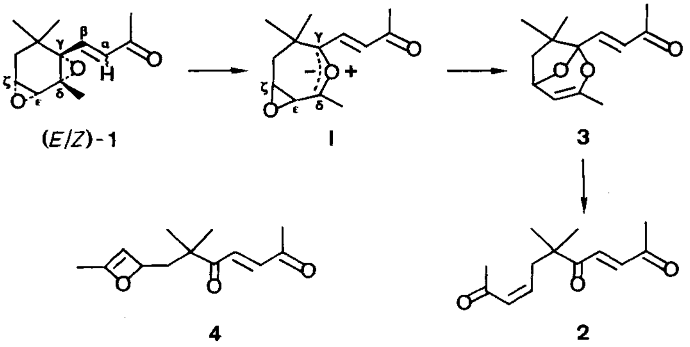
**1. Introduction.** – Recently we have shown that $^1\pi,\pi^*$-excitation of the epoxyenone (*E*)-**1** leads to the triketone **2** as the main product [2] (*Scheme 1*). Compounds of structure **3** and **4** were proposed as possible thermally labile intermediates. The present communication describes the isolation of compound **3** by low-temperature photolysis and chromatography, and proves its intermediacy in the formation of **2**.

*Scheme 1*



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[1]) 127th Communication, see [1].

**2. Results and discussion.** – Photolysis of a THF-solution of (*E*)-**1** at –78° ($\lambda$=254 mm, 45% conversion) gave (*Z*)-**1** (22%) and **3** (51%)[2]) after isolation by chromatography on $SiO_2$ at –78°.

The structure of compound **3** was determined from the spectral data.[3])

In particular, the enone side chain is evidenced in the UV.-spectrum by the maximum at 226 nm, as well as in the IR.-spectrum by the band at 1673 $cm^{-1}$. The presence of the dioxabicyclo[3.2.1]octene moiety is supported by the $^1H$-NMR.-spectrum including an *AB*-system at 2.00 ppm (*J*=13 Hz) for the 2 H–C(6'), a *m* at 4.35–4.62 ppm which is characteristic for the H–C(5') in geminal position to the ether O-atom and a broad *d* (*J*=5 Hz) at 4.96 ppm for the olefinic H–C(4') of the enol ether. Most of the evidence however stems from the $^{13}C$-NMR.-spectrum (see the *Figure*) exhibiting a *s* (148.8 ppm) and a *d* (102.8 ppm) for the enol ether moiety, as well as a *s* (108.3 ppm) which is characteristic for the acetal C-atom C(1').

On warming the NMR.-samples of **3** from –50° to +25°, the triketone **2** was obtained as the only product in quantitative yield.

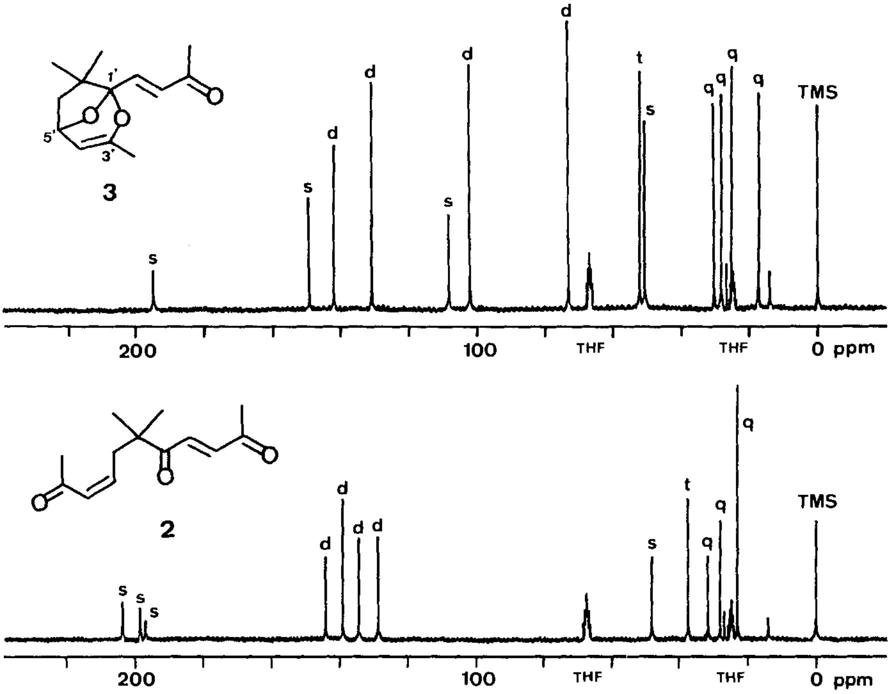

Figure. *$^{13}C$-NMR. spectra* (75 MHz, –50°, ($D_8$)THF) *of* **3** *and of* **2** *obtained on warming the sample of* **3** *to 25° for* ca. *30 min*

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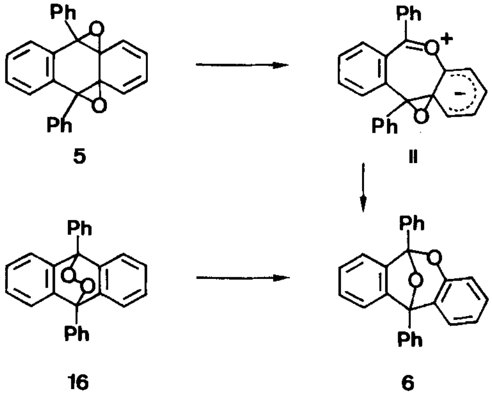
[2]) Yields are based on converted starting material.

[3]) Specific attempts to trap the intermediate **3** at –78° or above failed. On catalytic hydrogenation of the reaction mixture with various catalysts and at pressures up to 200 atm only hydrogenated **1** and **2** were obtained.

The formation of **3** presumably involves photolytic $C(\gamma),C(\delta)$-bond cleavage and subsequent 1,4-O-migration in the ylide intermediate **I**[4] *(Scheme 1).*

An analogous reaction mechanism was proposed for the photochemical rearrangement of the anthracene diepoxide **5** *via* **II** to **6** *(Scheme 2)* [4].

*Scheme 2*



Particularly interesting is the unexpected reactivity of compound **3**, since dioxabicyclo[3.2.1]octene systems of this type have been reported to be stable, even when the double bond is not a part of an aromatic ring[5] as in compound **6**.

For the transformation of **3** → **2**, an activation energy $E_a$ of $20.6 \pm 2.0$ kcal/mol was determined by measurement of the rate constants $k(T)$ at $-0.5°$, $9.8°$, $22.5°$ and $38.0°$ in $(D_8)$THF[6]. We have shown, that this process is not acid- or base-catalyzed by demonstrating the lack of effect of triethylamine or acetic acid on the measured rate of decomposition of **3** → **2**, leaving open only the possibility of a thermal electrocyclic ring opening as a likely mechanism for this reaction.

As possible explanation for the reactivity of **3**, it seems feasible that the additional enone side chain assists the cleavage of **3** → **2**. The corresponding compound **10** with a diene side chain, which was obtained among other products on photolysis of (*E*)-**11**, was found to be equally unstable rearranging to **12** [8] (see *Scheme 5*).

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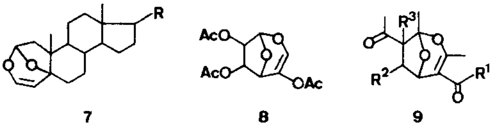
[4] On laser flash photolysis of (*E*)-**1**, ylide **I** has been detected showing a $\lambda_{max}$ at 620 nm and a lifetime $\tau$ of 30 ns at room temperature [3].

[5] Compare **7** [5], **8** [6] and **9** [7] (found in literature by CAS ONLINE substructure search (August 1982) for which we thank Dr. *E. Zass*).

*Scheme 3*

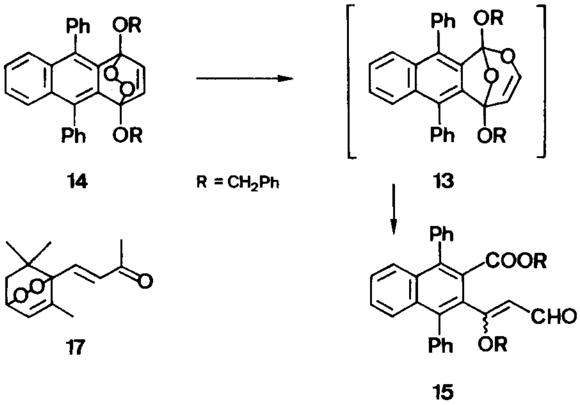


[6] Due to the small amounts of **3** available, we had to limit the kinetic studies to measurements at four different temperatures.

Thus, it seems likely that conjugation of the double bond with the $\pi$-system being formed rather than an inductive effect is involved in the stabilization of the transition state.

A similar conjugative effect may contribute to the instability of the postulated intermediate **13** in the thermal rearrangement of the anthracene endoperoxide **14**→**15** [9] *(Scheme 4)*.

*Scheme 4*



Thermal decomposition of the endoperoxide **16** led to the dioxabicyclo[3.2.1]-octene derivative **6**, which was already obtained on photochemical rearrangement of the diepoxide **5** [10] (see *Scheme 2*). On the basis of these findings it seems most likely that compound **3** is also the intermediate in the rearrangements of the endoperoxide **17** *(Scheme 4)* to the triketone **2** [2].

The behaviour of the diepoxides (*E*)-**1** and (*E*)-**11** was also investigated in the presence of *Lewis* acid. The reaction of the enone (*E*)-**1** and the diene (*E*)-**11** with $BF_3 \cdot OEt_2$ led to the acyclic products **18** and **19**, respectively *(Scheme 5)*. The diene (*E*)-**11** reacted at low temperature (−78°→0°) furnishing **19** in 85% yield. On the other hand, **2** was obtained only in 17% yield from the reaction of the enone (*E*)-**1** at room temperature, producing additionally the compound **20** in 5% yield[7]).

Acetals of type **6** are already reported to be products in the acid-catalyzed rearrangement of anthracene diepoxides of type **5** *(Scheme 2)* [12]. Thus, compounds **3** and **10** are feasible intermediates in the corresponding transformation of (*E*)-**1**→**18** and (*E*)-**11**→**19**, as we have shown that **3** and **10** cleave to **2** and **12** which are isomerized to **18** and **19**, respectively[8]). The different reactivity of the enone (*E*)-**1** and the diene (*E*)-**11** is indicative of the postulated reaction mechanism. Complexation of the *Lewis* acid at the $\varepsilon,\zeta$-epoxy function, followed by $C(\varepsilon)$,O- and $C(\gamma)$,$C(\delta)$-bond cleavage would lead to the dipolar intermediates **III** and **IV** which

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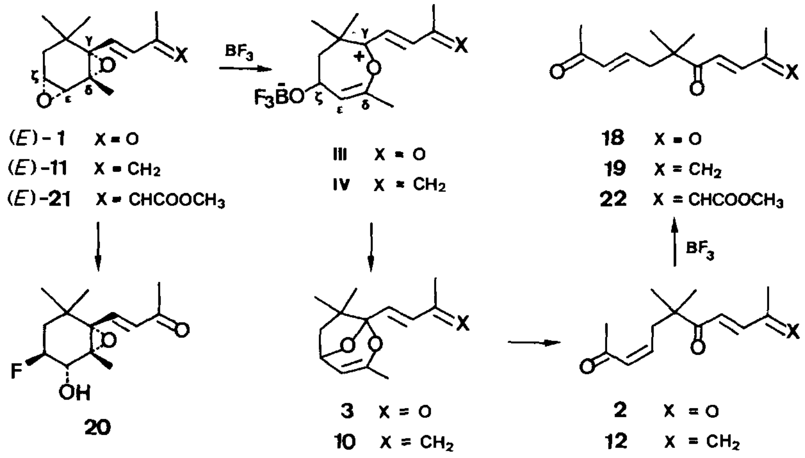
[7]) The transformations of (*E*)-**1**→**18** and (*E*)-**11**→**19** find precedent in the $BF_3 \cdot OEt_2$-rearrangement of the corresponding diepoxyester (*E*)-**21**→**22** *(Scheme 5)* [11].

[8]) On treatment of **2** with $BF_3 \cdot OEt_2$ **18** is obtained in quantitative yield.

Scheme 5



close to **3** and **10**, respectively. While in **IV** the diene side chain stabilizes the positive charge at C(γ), the enone does not have an equal stabilizing effect in intermediate **III**. In competition (*E*)-**1** undergoes opening of the ε,ζ-epoxy function by nucleophilic attack of fluoride at C(ζ), leading to **20**.

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## Experimental Part

*General.* See [2].

1. **Irradiation of (*E*)-*1* at low temperature.** – A solution of (*E*)-**1** (2.425 g, 10.9 mmol) in dry THF (100 ml) was irradiated with an air-cooled low-pressure Hg-lamp at –78° with stirring employing an external dry ice/acetone cooling bath. After 10 h of irradiation, the solvent was removed under high vacuum at –10°, the residue was chromatographed on a $SiO_2$-column which was cooled with dry ice, and the fractions were kept cold in a basin containing dry ice. The first fraction (0.550 g) was pure **3** according to NMR.-analysis and the second fraction gave on distillation (120°/0.02 Torr) a mixture (1.578 g) which consisted according to $^1$H-NMR.- and GC.-analysis of (*E*)-**1** (85%) and (*Z*)-**1** (15%). The yields of (*Z*)-**1** and **3**, based on converted starting material, are 22% and 51%, respectively.

*4-(3′,7′,7′-Trimethyl-2′,8′-dioxabicyclo[3.2.1]oct-3′-en-1′-yl)-3-buten-2-one* (**3**). – UV.: 226 (*ca.* 20000). – IR.: 3080*w*, 2970*s*, 2960*s S*, 2930*s*, 2863*s*, 1700*m*, 1673*s*, 1638*m*, 1611*w*, 1460*m*, 1445*m*, 1430*m*, 1379*s*, 1363*m*, 1355*s*, 1342*s*, 1312*m*, 1285*s*, 1272*m*, 1247*s*, 1200*m*, 1187*s*, 1165*m*, 1115*s*, 1065*m*, 1043*m S*, 1022*s*, 1000*m*, 979*s*, 971*s*, 948*m*, 935*w*, 911*m*. – $^1$H-NMR. (300 MHz, –50°, ($D_8$)THF): 0.94, 1.10 (2 *s*, 2 $H_3C$–C(7′)); 1.73 (*s*, $w_{1/2}=3$, $H_3C$–C(3′)); 2.00 (*AB*-system, $J=13$, $\delta_A=1.90$, broadened, $\delta_B=2.10$, 2 H–C(6′)); 2.26 (*s*, 3 H–C(1)); 4.35–4.62 (*m*, H–C(5′)); 4.96 (*d*, $J=5$, broadened, H–C(4′)); 6.62 (*AB*-system, $J=16$, $\delta_A=6.49$, $\delta_B=6.76$, H–C(3), H–C(4)). – $^{13}$C-NMR. (75 MHz, –50°, ($D_8$)THF): 18.7, 25.3, 27.0, 30.1 (4 *qa*, 4 $CH_3$); 52.0 (*t*, C(6′)); 73.8 (*d*, C(5′)); 102.8 (*d*, C(4′)); 131.0, 141.2 (2 *d*, C(3), C(4)); 50.6 (*s*, C(7′)); 108.3 (*s*, C(1′)); 148.8 (*s*, C(3′)); 197.8 (*s*, C(2)).

**2. Thermolysis of 3.** – A solution of **3** (*ca.* 200 mg) in ($D_8$)THF (2 ml) was divided to equal volumes in four NMR.-tubes at −78°. The samples were warmed to −0.5°, 9.8°, 22.5° and 38°, respectively. Periodically, the course of the reaction was checked by NMR. at −80°, measuring the integral in the olefinic region. At the four temperatures, three to six measurements were made to determine the values of $k$(T) from the gradient of the plot of relative concentration against time: $k(-0.5°) = 0.178 \cdot 10^{-4}$, $k(9.8°) = 0.442 \cdot 10^{-4}$, $k(22.5°) = 2.13 \cdot 10^{-4}$, $k(38°) = 19.25 \cdot 10^{-4}$ mol sec$^{-1}$.

From the gradient of the plot of the values ln $k$(T) against 1/T, $E_a$ was determined to be 20.6 ± 2.0 kcal/mol.

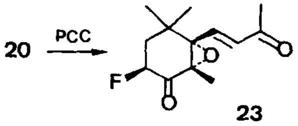
**3. Acid-catalyzed rearrangements.** – 3. 1. *Reaction of* (E)-**1** *with* $BF_3 \cdot OEt_2$. To a solution of (*E*)-**1** (1.17 g, 5.27 mmol) in benzene (80 ml), was added slowly $BF_3 \cdot OEt_2$ (0.5 ml, 3.96 mmol) at ambient temperature. After stirring for 1 h, workup and subsequent chromatography ($SiO_2$, ether/pentane 2:1) yielded recovered (*E*)-**1** (110 mg, 9%), **18** [2] (204 mg, 17%) and **20** (65 mg, 5%).

*(*E*, 1'*R**, 4'*R**, 5'*R**, 6'*S**)-4-(4'-Fluoro-5'-hydroxy-2',2',6'-trimethyl-7'-oxabicyclo[4.1.0]hept-1'-yl)-3-buten-2-one* (**20**). M.p. 103° (ether/pentane). – UV. (0.188 mg in 10 ml EtOH): 228 (12400), end absorption to 380. – IR. ($CHCl_3$): 3605*m*, 3550*m*, 3450*m* br., 3030*w*, 2960*s*, 2940*s*, 2898*m*, 2870*m S*, 1685*m S*, 1670*s*, 1622*s*, 1445*m*, 1375*m S*, 1360*s*, 1340*m S*, 1300*m*, 1282*m*, 1030*s*, 1005*m S*, 978*s*, 955*w*, 930*w*, 895*w*, 875*m*. – $^1$H-NMR. (300 MHz, $CDCl_3$): 1.00, 1.34 (2*s*) and 1.22 (*d*, $J = 1.7$, 2 $H_3C-C(2')$, $H_3C-C(6')$); 1.55–1.80 (*m*, 2 H–C(3)); 2.25–2.29 (*m*, OH); 2.29 (*s*, 3 H–C(1)); 3.87–3.91 (*m*, H–C(5')); 4.55 ($d \times d \times d \times d$, $J_1 = 48.6$, $J_2 = 7.7$, $J_3 = 4.7$, $J_4 = 3.2$, H–C(4')); 6.64 (*AB*-system, $J = 15.7$, $\delta_A = 6.31$, $\delta_B = 6.98$, H–C(3), H–C(4)). – $^{13}$C-NMR.: 16.8, 25.6, 28.1, 28.2, 28.3 (5 *qa*, 4 $CH_3$); 38.9 (*t*, split into *d*, $J = 18.0$, C(3')); 72.8 (*d*, split into *d*, $J = 26.8$, C(5')); 91.3 (*d*, split into *d*, $J = 171.2$, C(4')); 133.3, 140.3 (2 *d*, C(3), C(4)); 34.2 (*s*, split into *d*, $J = 5.9$, C(2')); 67.9, 68.1 (*s*, split into *d*, $J = 5.6$, C(6')); 72.3 (*s*, C(1')); 197.3 (*s*, C(2)). – MS.: *123* (100), 43 (49).

$C_{13}H_{19}FO_3$ (242.27) Calc. C 64.44 H 7.90 F 7.84% Found C 64.44 H 7.92 F 7.66%

For the assignment of the couplings in the $^1$H-NMR.-spectrum the hydroxy compound **20** was oxidized to **23**: to a solution of **20** (22 mg, 0.09 mmol) in $CH_2Cl_2$ (5 ml) was added PCC (270 mg, 1.25 mmol). After stirring for 18 h, the mixture was worked up and chromatographed to give **23** (12 mg, 55%).

*Scheme 6*



*(*E*, 1'*R**, 4'*R**, 6'*R**)-4-(4'-Fluoro-2',2',6'-trimethyl-5'-oxo-7'-oxabicyclo[4.1.0]hept-1'-yl)-3-buten-2-one* (**23**). B.p. 120°/0.04 Torr. – IR.: 3010*w*, 2965*s*, 2935*m*, 2895*w S*, 2875*m*, 1735*s*, 1700*s*, 1680*s*, 1628*s*, 1465*m*, 1450*m*, 1425*m*, 1395*m*, 1382*m*, 1370*m*, 1358*s*, 1300*s*, 1262*m*, 1245*s*, 1230*m*, 1190*m*, 1165*m S*, 1161*m*, 1145*m S*, 1120*w*, 1070*m*, 1065*m*, 1032*m*, 978*s*, 940*m S*, 935*m*, 915*w*, 900*m*, 891*m*, 862*w*. – $^1$H-NMR. (300 MHz, $CDCl_3$): 1.09, 1.17 (2*s*) and 1.35 (*d*, $J = 0.5$, 2 $H_3C-C(2')$, $H_3C-C(6')$); 1.78 ($d \times d \times d$, $J_1 = 27.4$, $J_2 = 14.8$, $J_3 = 4.1$, H–C(3')); 2.31 (*s*, 3 H–C(1)); 2.50 ($d \times d \times d$, $J_1 = 22.8$, $J_2 = 14.8$, $J_3 = 8.6$, H–C(6')); 5.19 ($d \times d \times d$, $J_1 = 50.0$, $J_2 = 8.6$, $J_3 = 4.1$, H–C(5')); 6.61 (*AB*-system, $J = 15.6$, $\delta_A = 6.32$, $\delta_B = 6.90$, H–C(3), H–C(4)). – MS.: *123* (100), 43 (64).

3.2. *Reaction of* **2** *with* $BF_3 \cdot OEt_2$. A solution of **2** (411 mg, 1.85 mmol) in dry ether (20 ml) was cooled to −18°, and $BF_3 \cdot OEt_2$ (0.4 ml, 3.17 mmol) was added dropwise with stirring. The solution was allowed to warm to r.t., stirred for an additional hour and worked up to yield **18** [2] (391 mg, 95%) which was pure according to $^1$H-NMR.-analysis.

3.3. *Preparation of* (E)-**11**. A solution of methylenetriphenylphosphorane (*ca.* 0.2 M) in ether was added slowly to a solution of (*E*)-**1** (7.07 g, 31.8 mmol) in ether (200 ml) until all starting material was consumed (TLC. control). The reaction mixture was diluted with pentane (300 ml) and filtered through $SiO_2$. Removal of the solvent and distillation of the residue (100°, 0.05 Torr) yielded (*E*)-**11** (5.27 g, 75%).

*(E,1'R*,2'S*,3'S*,4'S*)-4-(1',2':3',4'-diepoxy-2',6',6'-trimethyl-1'-cyclohexyl)-2-methyl-1,3-butadiene* ((*E*)-**11**). B.p. 100°/0.05 Torr. – UV. (0.709 mg in 50 ml EtOH): 235 (22650). – IR.: 3080*w*, 3030*w S*, 2990*m*, 2960*s*, 2920*s*, 2890*m*, 2870*m*, 1788*w*, 1607*m*, 1460*m*, 1445*s*, 1430*m*, 1385*m*, 1375*s*, 1362*s*, 1320*w*, 1310*w*, 1255*m*, 1198*w*, 1185*w*, 1155*w*, 1130*w*, 1118*w*, 1075*m*, 1058*m*, 1025*m*, 1010*w*, 990*m*, 970*s*, 960*m*, 942*m*, 900*s*, 890*s*, 852*m*, 846*m*. – $^1$H-NMR.: 0.86, 1.08, 1.34 (3 *s*, $H_3C{-}C(2')$, 2 $H_3C{-}C(6')$); 1.30-1.75 (*m*, 2 $H{-}C(5')$); 1.82 (*d*, $J = 1$, $H_3C{-}C(2)$); 2.70-2.94 (*m*, $H{-}C(3')$, $H{-}C(4')$); 4.96 (*m*, $w_{1/2} = 4$, 2 $H{-}C(1)$); 5.95 (*AB*-system, $J = 16$, $\delta_A = 5.67$, $\delta_B = 6.23$, $H{-}C(3)$, $H{-}C(4)$). – $^{13}$C-NMR.: 18.2, 18.5, 24.4, 26.7 (4 *qa*, 4 $CH_3$); 35.7 (*t*, C(5')); 117.0 (*t*, C(1)); 46.7, 52.1 (2 *d*, C(3'), C(4')); 122.2, 136.4 (2 *d*, C(3), C(4)); 35.4 (*s*, C(6')); 60.3, 69.7 (2 *s*, C(1'), C(2')); 140.7 (*s*, C(2)). – MS.: 220 (13, $M^+$, $C_{14}H_{20}O_2$), 177 (28), 136 (10), 125 (16), 121 (28), 107 (18), 105 (22), 96 (12), *95* (100), 93 (48), 91 (18), 77 (13), 67 (22), 43 (58), 41 (22).

$C_{14}H_{20}O_2$ (220.31) Calc. C 76.32 H 9.14% Found C 76.24 H 9.09%

3.4. *Reaction of (E)-**11** with $BF_3 \cdot OEt_2$.* To a solution of (*E*)-**11** (2.07 g, 9.4 mmol) in ether (20 ml) was added dropwise at –78° $BF_3 \cdot OEt_2$ (1.3 ml, 10.3 mmol). The solution was allowed to warm to 0°, was then quenched by the addition of water and worked up in ether. Chromatography on $SiO_2$ (ether/pentane 11:1) afforded **19** (1.77 g, 85%).

*6,6,10-Trimethyl-3,8,10-undecatrien-2,7-dione* (**19**). B.p. 100°/0.02 Torr. – UV. (0.192 mg in 20 ml pentane): 219 (12500), 264 (18100). – UV. (1.934 mg in 2 ml pentane): 366 (100), end absorption to 410. – IR.: 3090*w*, 3060*w*, 3040*w*, 2970*m*, 2930*m*, 2900*w S*, 2885*w*, 1820*w*, 1700*m S*, 1685*s S*, 1680*s*, 1630*s*, 1625*s*, 1592*s*, 1468*m*, 1460*m S*, 1450*m*, 1435*m*, 1425*m S*, 1388*m*, 1375*m*, 1365*m S*, 1360*m*, 1328*m S*, 1320*m*, 1268*m*, 1250*s*, 1220*w*, 1180*w*, 1160*w*, 1140*w*, 1080*m S*, 1070*m*, 1050*m*, 1025*w*, 1010*w*, 982*s*, 940*w*, 910*m*, 885*w*, 860*w*. – $^1$H-NMR. (80 MHz, $CDCl_3$): 1.22 (*s*, 2 $H_3C{-}C(6)$); 1.96 (*m*, $w_{1/2} = 2.6$, $H_3C{-}C(10)$); 2.22 (*s*, 3 $H{-}C(1)$); 2.49 (*d*, $J = 7$, 2 $H{-}C(5)$); 5.45 (*m*, $w_{1/2} = 4$, 2 $H{-}C(11)$); 6.38 (*AB*-system, $J = 16$, $\delta_A = 6.06$, $H{-}C(3)$, $\delta_B = 6.71$, split into *t*, $J = 7$, $H{-}C(4)$); 6.95 (*AB*-system, $J = 15$, $\delta_A = 6.50$, $\delta_B = 7.40$, $H{-}C(8)$, $H{-}C(9)$). – $^{13}$C-NMR. (~80% pure): 18.1, 24.3, 26.7 (4 *qa*, 2 *qa* at 24.3, 4 $CH_3$); 42.0 (*t*, C(5)); 125.4 (*t*, C(11)); 120.8, 133.9, 143.8, 145.9 (4 *d*, C(3), C(4), C(8), C(9)); 46.5 (*s*, C(6)); 140.7 (*s*, C(10)); 197.7, 202.4 (2 *s*, C(2), C(7)). – MS.: 220 (14, $M^+$, $C_{14}H_{20}O_2$), 177 (28), 105 (41), *93* (100), 92 (22), 91 (16), 77 (15), 43 (24).

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