HETEROCYCLES, Vol. 11, 1978

PHOTOINDUCED OXIRANE-CLEAVAGE OF A CONJUGATED ε,ζ-EPOXY-DIENONE[1]

Veronica Scherrer, Hans Richard Wolf und Oskar Jeger*
Laboratorium für Organische Chemie der Eidg. Technischen
Hochschule, 8092 Zürich, Switzerland

Dedicated to Professor S.Nozoe on the occasion of his
77th birthday.

On UV.-irradiation the conjugated epoxydienone 2 undergoes oxirane-cleavage by scission of the C,O or C,C-bond and forms the isomeric products 9-12. Thus evidence is given that dienones can react via photoinduced β-cleavages.

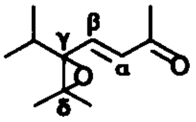
In competition to these processes E/Z-isomerization and dimerization of the dienone moiety of 2 is observed (2→14,15 and 2→16).

Introduction.-Continuing our studies of the photochemistry of conjugated unsaturated ketones (2) we recently reported on the pho-

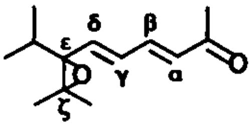
---

[1] Photochemical Reactions; 96th communication (1).

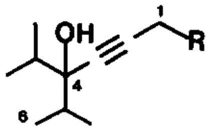
toinduced vinylogous β-cleavage of the α,β-unsaturated γ,δ-epoxyketone 1(3). This epoxy-enone shows cleavage of the C(γ),C(δ)-bond exclusively on π,π*-excitation, but it gives cleavage of the C(γ),O-bond on n,π*-excitation. Compared with these oxirane-cleavages, the E/Z-isomerization of the enone moiety is, rather unexpectedly, a minor photoprocess(2). We therefore decided to check the photochemistry of the analogous conjugated epoxy-dienone 2.



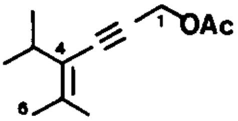
1



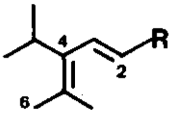
2



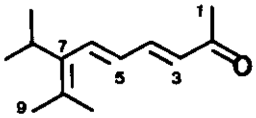
3 R=OH **4** R=OAc



5



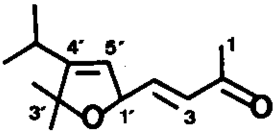
6 R=CH_2OH **7** R=CHO



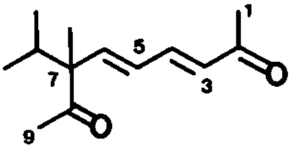
8

Synthesis of 2.-Grignard condensation of 3-hydroxypropyne with diisopropylketone gave the diol 3(88%). Treatment with Ac_2O/pyridine converted 3 to the monoacetate 4(93%). Dehydration of 4 by $POCl_3$/pyridine yielded 5(76%). Reduction of 5 by $LiAlH_4$/ether gave the dienol 6(92%), which was converted by MnO_2-oxidation to the aldehyde 7 (86%). Condensation of 7 with acetone in aqueous NaOH, followed by column chromatography (SiO_2, ether-pentane-hexane-(1:1:1)), yielded the trienone 8(75%). Epoxydation of 8 with MCPBA under standard conditions (3) gave 2(74%).

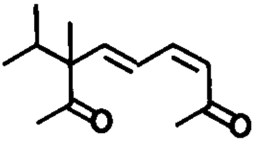
UV.-irradiations.-a) 2 was irradiated in pentane (500ml, $5{,}8\cdot10^{-2}M$) at λ=254nm (Hg-low pressure lamp(3),quartz) to 80% conversion. After evaporation of the solvent,column chromatography (SiO_2,ether-pentane-hexane(1:1:1)) yielded mixtures of enriched products, whose distribution has been estimated (by combination of gas-chromatography (11% QF-1,180°) and PMR-spectroscopy) to be: 1% 9,6% 10,0,5% 11,6% 12,4% 13 (13 is proven to be a hydrolysis product of 12),4% 14,14% 15 and 17% 16.



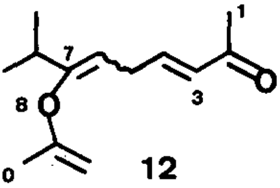
9



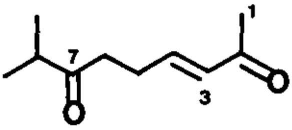
10



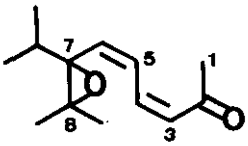
11



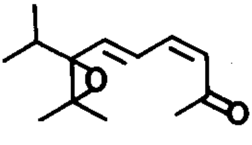
12



13

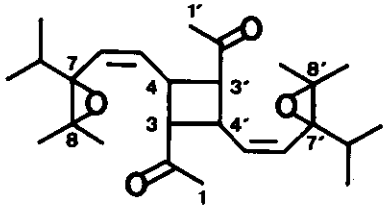


14

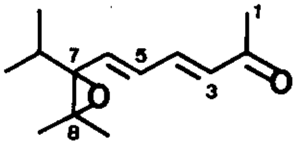


15

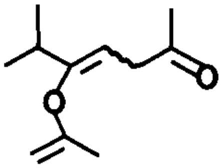
b) 2 was irradiated in pentane (500ml, $4{,}4\cdot10^{-2}M$) at λ>347nm (Hg-medium pressure lamp(3),NaBr/$Pb(NO_3)_2$-filter(3)) to 80% conversion. The photolysis mixture was worked up and analyzed as in experiment a).Distribution of products: 7% 9,7% 10,0,5% 11,traces of 12, 1% 14,6% 15 and 45% 16.



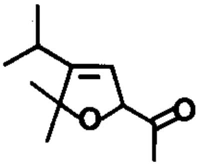
16



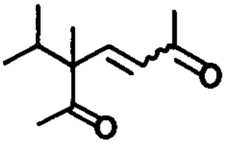
2



17



18



19

Discussion.- UV.-irradiation of the conjugated epoxydienone 2 leads to four different reactions: scission of the oxirane by cleavage of the C(7),O-bond (2→9,10,11),cleavage of the C(7),C(8)-bond (2→12),E/Z-isomerization of the dienone (2→14,15) and enone-dimerization (2→16).In regard to the photocleavages 2 shows a similar excitation dependence as the epoxyenone 1.Thus,the amount of C,O-bond cleavage is about 8% on π,π^*-excitation,but 20% on n,π^*-excitation (1:18% versus 96%(3)).On the other hand,C,C-bond cleavage amounts to about 10% at λ=254nm,whereas at λ>347nm it is virtually absent(1:65% versus nil(3)).The isomerization 2→12 is an homosigmatropic 1,5-H-shift analogous to the isomerization 1→17(see(2)(3)). On the other hand the isomerizations 2→9,10,11 parallel the photoisomerizations 1→18,19 (for discussion see(3)).On contrast to 1 the epoxydienone 2 shows E/Z-isomerization as well as dimerization of the unsaturated carbonyl system without oxirane scission, both on π,π*-and n,π*-excitation.We conclude that an excited acyclic epoxydienone of type 2 shows preferentially dimerization and E/Z-isomerization of the dienone moiety.However,it may also react by scission of the oxirane system thus supporting the presumption that acyclic dienones can undergo photoinduced β-cleavages.

Analytical data.-IR and PMR(100MHz) spectra were recorded in CCl_4,CMR(25,2MHz) spectra in $CDCl_3$ and UV spectra in pentane. 2[2]: bp.85-90°/0,08mm Hg; λ_{max} 270(25860); ν_{max} 1692,1673,1631, 1597cm^{-1}; δ(PMR) 0.95,1.03(2d,J=7,$(\underline{H_3}C)_2$CH-C(7)),1.12,1.35(2s, H_3C-C(8),3H-C(9)),1.74(septet,J=7,$(H_3C)_2\underline{CH}$-C(7)),2.14(s,3H-C(1)), 5.96-6.44(m,H-C(3),-C(4),-C(6)),7.02(dxdxd,J=16,J=9,J=2,H-C(5)[3]); δ(CMR) 65.0,71.3(2s,C(7),C(8));m/e 208(34,M^+),193(53). 3[2]: mp.77-79°; ν_{max} 3620,3400b cm^{-1}; δ 0.94,0.97(2d,J=6,$(\underline{H_3}C)_2$CH-C(4), H_3C-C(5),3H-C(6)),1.60-2.34(2septet,J=6,H-C(5),$(H_3C)_2\underline{CH}$-C(4) and 2bs,HO-C(1),HO-C(4)),4.19(s,2H-C(1));m/e 127(90,M^+-43). 4[2]: bp. 115°/0,008mm Hg; ν_{max} 3621,3490b,1747cm^{-1}; δ 1.74(s,HO-C(4)),

---

[2] Correct C,H values in microanalysis were obtained.

[3] The assignment is based on comparison with the corresponding d_4-deuterated compound (d_3 at C(1); d_1 at C(3)).The deuteration (d_4>95%) was achieved by condensation of 7 with acetone-d_6 in D_2O/NaOD.

1.87(2septets,J=6,$(H_3C)_2\underline{CH}$-C(4),H-C(5)),2.00(s,H_3CCOO-C(1)),4.58 (s,2H-C(1)); m/e 169(100,M^+-43). 5: purity about 95%; bp.50-55°/ 0,06mm Hg; ν_{max} 1748cm^{-1}; δ 0.98(d,J=7,$(\underline{H_3}C)_2$-CH-C(4)),1.74,1.87 (2s,H_3C-C(5),3H-C(6)),2.00(s,H_3CCOO-C(1)); m/e 194(17,M^+). 6: bp. 50-55°/0,08mm Hg; λ_{max} 239(8770); ν_{max} 3620,3345b,3015,1635,1000, 973cm^{-1}; δ 4.06(d,J=6,2H-C(1)),5.52(dxt,J=16,J=6,H-C(2)),6.01(bd, J=16,H-C(3)); m/e 154(73,M^+),121(71),111(100). 7: bp.35-40°/0,06mm Hg; ν_{max} 1685,1608cm^{-1}; δ 1.08(d,J=7,$(\underline{H_3}C)_2$CH-C(4)),1.86(2s,H_3C-C(5),3H-C(6)),2.98(septet,J=7,$(H_3C)_2\underline{CH}$-C(4)),6.04(dxd,J(2,3)=16, J(2,1)=7.5,H-C(2)),7.14(d,J(3,2)=16,H-C(3)),9.42(d,J(1,2)=7.5, H-C(1)); m/e 152(13,M^+),137(100). 8: bp.95-100°/0,15mm Hg; λ_{max} 313(25500); ν_{max} 1685,1668,1610,1590cm^{-1}; δ 1.04(d,J=7,$(\underline{H_3}C)_2$CH-C(7)),1.78(2s,H_3C-C(8),3H-C(9)),2.14(s,3H-C(1)),2.91(septet,J=7, $(H_3C)_2\underline{CH}$-C(7)),5.98(d,J(3,4)=16,H-C(3)[3]),6.15(dxd,J(5,6)=16,J(5,4)= 10,H-C(5)[3]),6.54(bd,J(6,5)=16,H-C(6)[3]),7.03(dxd,J(4,3)=16,J(4,5)= 10,H-C(4)[3]); m/e 192(45,M^+),177(24),149(100). 9[4]: bp.80-85°/0,1mm Hg.; λ_{max} 218(16700); ν_{max} 1698,1676,1630,1072,1045,1035cm^{-1}; δ(PMR) 1.11(d,J=7,$(\underline{H_3}C)_2$CH-C(4')),1.27,1.32(2s,2 H_3C-C(3')),2.15 (s,3H-C(1)),5.15(bd,J(1',4)=6,H-C(1')[3]),5.27(bs,H-C(5')[3]), 6.28 (AB-system,δ_A=6,06,δ_B=6,49,J=16,A-part d,J=2,B-part d,J=6,H-C(3), H-C(4)); δ(CMR) 26.0(d,$(H_3C)_2\underline{CH}$-C(4')),82.1(d,C(1')),117.7,129.0

---

[4] 2 was treated with $BF_3O(C_2H_5)_2$ in benzene. Column chromatography (SiO_2,ether-pentane-hexane-(1:1:1)) yielded 32% 9 (used for spectral analysis) and 28% 10.

147.2 (3d,C(3),C(4),C(5')),89.7(s,C(3')),155.8(s,C(4')),198.1(s, C(2)); m/e 208(44,M$^+$). $\underline{10}$[2,3]: bp.110-115°/0,01mm Hg; λ_{max} 261sh (26140),268(29160); ν_{max} 1705,1695,1670cm^{-1}; δ(PMR in CDCl$_3$) 0.81, 0.84(2d,J=7,($\underline{H_3}$C)$_2$CH-C(7)),2.10,2.25(2s,3H-C(9),3H-C(1)),6.00-6.42 (m,H-C(3),-C(4),-C(6)),6.98-7.32(m,H-C(5)); δ(CMR) 34.0(d, (H$_3$C)$_2$$\underline{CH}$-C(7)),58.6(s,C(7)),198.3,209.4(2s,C(2),C(8)); m/e 208 (1,M$^+$),166(78). $\underline{11}$: λ_{max} 270(20670),278(20840); ν_{max} 1710,1687, 1622,1578cm^{-1}; δ 0.97,0.81(2d,J=7,($\underline{H_3}$C)$_2$CH-C(7)),2.02,2.11(2s, 3H-C(9),3H-C(1)),5.91(d,J(3,4)=11,H-C(3)),6.02(d,J(6,5)=16, H-C(6)),6.32(dxd appearing as t,J(4,5)=J(4,3)=11,H-C(4)[3]),7.45 (dxd,J(5,6)=16,J(5,4)=11,H-C(5)); m/e 208(1,M$^+$),166(88). $\underline{12}$: (obtained together with $\underline{14}$; column chromatography of the (1:1)-mixture over a layer of (COOH)$_2$ on SiO$_2$ in ether-pentane-hexane-(1:1:1) gave a (1:1)-mixture of $\underline{13}$ and $\underline{14}$, which was separated by vpc.) δ 1.04(d,J=7,($\underline{H_3}$C)$_2$CH-C(7)),1.84(s,H$_3$C-C(9)),2.10(s, 3H-C(1)),2.42 (septet,J=7,(H$_3$C)$_2$$\underline{CH}$-C(7)),2.80(dxd appearing as t, J(5,6)=J(5,4)=6,2H-C(5)),3.85(bs,2H-C(10)),4.91(t,J(6,5)=6,H-C(6)), 5.72-6.12(m,H-C(3),overlapped by signals of $\underline{14}$),6.61(dxt,J(4,3)= 16,J(4,5)=6,H-C(4)). $\underline{13}$: λ_{max} 218(13620); ν_{max} 1715,1702,1675, 1625cm^{-1}; δ(PMR) 1.06(d,J=7,H$_3$C-C(8),3H-C(9)),2.10(s,3H-C(1)), 6.32(AB-system,δ_A=5.94,δ_B=6.68,J=17,B-part d,J(4,5)=6,H-C(3)[3], H-C(4)); δ(CMR) 18.2(2q,C(9),H$_3$$\underline{C}$-C(8)),26.9(q,C(1)),26.3,38.2(2t, C(5),C(6)),40.8(d,C(8)),131.7,146.7(2d,C(3),C(4)),198.2,212.7(2s, C(2),C(7)); m/e 168 (27,M$^+$). $\underline{14}$: λ_{max} 274(16920); ν_{max} 1685,1623, 1570cm^{-1}; δ 0.94,0.97(2d,J=7,($\underline{H_3}$C)$_2$CH-C(7)),1.16,1.22(2s,H$_3$C-

C(8),3H-C(9)),1.69(septet,J=7,(H_3C)$_2$CH-C(7)),2.10(s,3H-C(1)),5.79 (d,J(6,5)=11,H-C(6)),5.91(d,J(3,4)=11,H-C(3)[3]),7.00(dxd appearing as t,J(4,3)=J(4,5)=11,H-C(4)),7.43(dxd appearing as t,J(5,4)= J(5,6)=11,H-C(5)); m/e 208(7,M^+). 15: λ_{max} 275(23400); ν_{max}1692, 1666,1628,1580cm^{-1}; δ 0.92,1.03(2d,J=7,(H_3C)$_2$CH-C(7)),1.16,1.36 (2s,H_3C-C(8),3H-C(9)),1.74(septet,J=7,(H_3C)$_2$CH-C(7)),2.14(s, 3H-C(1)),5.88(d,J(3,4)=11,H-C(3)[3],overlapped by d at 6.01),6.01 (d,J(6,5)=16,H-C(6)),6.30(dxd appearing as t,J(4,3)=J(4,5)=11, H-C(4)),7.31(dxd,J(5,6)=16,J(5,4)=11,H-C(5)); m/e 208(12,M^+). 16: mixtures of stereoisomers; bp.190-200°/0,05mm Hg; ν_{max} 1708cm^{-1}; δ(PMR) 1.31(s,H_3C-C(8),H_3C-C(8')),1.44-1.86(b septet,(H_3C)$_2$CH-C(7), -C(7')),1.98,2.00(2s appearing in the ratio of 1:3,3H-C(1)[3], 3H-C(1')[3]),2.42-2.72(m,H-C(3)[3],H-C(3')[3]),2.99-3.20(m,H-C(4)[3], H-C(4')[3]),5.46-5.76(m,C(5),-C(5'),-C(6),-C(6')); CMR shows 10q and δ 31.0(2d,(H_3C)$_2$CH-C(7),-C(7')),45.0,45.2,45.4,49.8,50.1(d, C(3),C(3'),C(4),C(4')),126.2,134.1(2x2d,C(5),C(5'),C(6),C(6')), 64.2,70.9(2x2s,C(7),C(7'),C(8),C(8')),206.4(2s,C(1),C(1')); m/e 416(2,M^+),373(10),303(18),208(44),207(24),193(26),166(34).

Acknowledgments.-Financial support by the Swiss National Fund for the Advancement of Scientific Research and by Ciba-Geigy AG, Basel, is gratefully acknowledged.

REFERENCES

1. 95th commun.: A.K.Dey and H.R.Wolf, Helv.Chim.Acta, 1978, **61**, 626.
2. B.Frei, H.Eichenberger, B. von Wartburg, H.R.Wolf and O.Jeger, Helv.Chim.Acta, 1977, **60**, 2968.
3. H.Eichenberger, H.R.Wolf and O.Jeger, Helv.Chim.Acta, 1976, **59**, 1253.

Received, 25th July, 1978