297. Photochemical Reactions

80th Communication [1]

Preliminary Report on the Photolysis of (*E*)-Dehydro-*β*-ionone-epoxide

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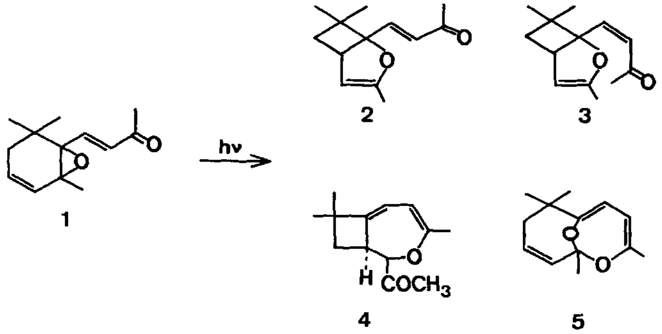
Summary. Irradiation of a pentane solution of (*E*)-dehydro-*β*-ionone-epoxide (**1**) with light from a medium pressure mercury lamp using acetone as filter led to formation of the *isomers* **2**, **3**, **4** and **5** by novel photochemical processes.

Irradiation of a 0.04 m pentane solution of (*E*)-dehydro-*β*-ionone-epoxide (**1**) [2] using medium pressure mercury lamp and acetone as filter led to a mixture of products consisting mainly of the *isomers* **2**, **3**, **4** and **5** shown in *Scheme 1* ²). The structures assigned were inferred from spectroscopic data and confirmed by degradation³).

Scheme 1



The dihydrofurane grouping of *isomer* **2** [b.p.: 75–80°/0.05 Torr; IR. (CCl_4): 1700, 1680, 1670, 1625 cm⁻¹; NMR. (CCl_4): $\delta = 1.12$ (*s*, 3); 1.17 (*s*, 3); 1.64 (*d*×*d*, $J_1 = 11.5$, $J_2 = 4.5$; 1); 1.96 (*d*×*d*, $J_1 = 11.5$, $J_2 = 8$; 1); 1.83 (*t*, $J = 1$; 3); 2.21 (*s*, 3); 3.21 (br. *m*, w/2 = 14; 1); 4.64 (narrow *m*, w/2 = 6; 1); 6.16 (*d*, $J = 16$; 1); 6.86 (*d*, $J = 16$; 1); UV. (EtOH): 226 nm ($\varepsilon = 13700$)] was cleaved oxidatively by successive

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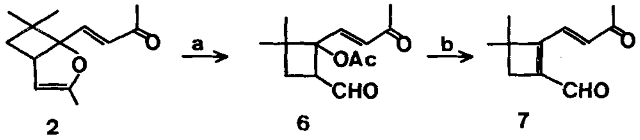
²) Irradiation of **1** in pentane with a low pressure lamp in quartz apparatus ($\lambda = 254$ nm) until 50% conversion gave **2** as the only major product. Subsequent irradiation did not increase the yield of **2** but led to a more complex reaction mixture.

³) Isomers **2**–**5** gave correct analyses for $C_{13}H_{18}O_2$ and mass spectra in accord with the proposed structures.

treatment with aqueous methanolic $NaIO_4$ and ethereal H_5IO_6 solutions[4]. The resulting unstable *acetate* **6** was not isolated in analytically pure form [IR. (CCl_4): 2735, 1745, 1725, 1684, 1632 cm^{-1}; NMR. (CCl_4): $\delta = 1.10$ (*s*, 3); 1.16 (*s*, 3); 1.66 ($d \times d$, $J_1 = 12$, $J_2 = 9$; 1); 2.08 (*s*, 3); 2.28 (*s*, 3); 2.33 ($d \times d$, $J_1 = 12$, $J_2 = 7$; 1); 3.54 (*t*-like *m*, $J = 7$; 1); 6.06 (*d*, $J = 16$; 1); 6.90 (*d*, $J = 16$; 1); 9.66 (*d*, $J = 1$; 1)]. It readily lost acetic acid during chromatography on silica gel to give the *aldehyde* **7** [m.p.: 51–55° (from pentane at –30°); $m/e = 178$; IR. (CCl_4): 2750, 2720, 1675 (very strong), 1620, 1575 cm^{-1}; NMR. ($CDCl_3$): $\delta = 1.39$ (*s*, 6); 2.39 (*s*, 3); 2.50 (*s*, 2), 6.34 and 7.36 (*AB*, $J = 16$; 2); 9.90 (*s*, 1); UV. (EtOH): 298 nm ($\varepsilon = 26900$)].

Scheme 2



a: $NaIO_4/H_5IO_6$ b: $-CH_3COOH$

The structure of **3** as a *stereoisomer of* **2**, differing only in the configuration of the α,β-unsaturated ketone moiety, was assigned by comparison of spectroscopic and chemical properties[5]: **3** [b.p.: 75–80°/0.05 Torr; IR. (CCl_4): 1710, 1670, 1622 cm^{-1}; NMR. (CCl_4): $\delta = 1.12$ (*s*, 3); 1.17 (*s*, 3); 1.57 ($d \times d$, $J_1 = 11$, $J_2 = 4.5$; 1); 2.02 ($d \times d$, $J_1 = 11$, $J_2 = 8.5$; 1); 1.75 (*t*, $J = 1$; 3); 2.19 (*s*, 3); 3.18 (br. *m*, w/2 = 16; 1); 4.64 (narrow *m*, w/2 = 6; 1); 5.78 and 5.93 (*AB*, $J = 12$; 2); UV. (pentane): 213,5 nm ($\varepsilon = 9330$)].

The *dihydrooxepine derivative* **4** [b.p.: 74°/0.03 Torr; IR. (CCl_4): 1730, 1629 cm^{-1}; NMR. (CCl_4): $\delta = 1.13$ (*s*, 3); 1.24 (*s*, 3); 1.88 ($d \times d$, $J_1 = 11$, $J_2 = 9$; 1); 1.92 (*s*, 3); 2.14 (*s*, 3); 2.44 ($d \times d$, $J_1 = 11$, $J_2 = 7$; 1); 3.32 (br. *m*, w/2 = 17; 1); 4.58 (*d*, $J = 4.5$; 1); 4.79 (broadened *d*, $J = 7$; 1); 5.22 ($d \times d$, $J_1 = 7$, $J_2 = 3$; 1); UV. (pentane): 266.5 nm ($\varepsilon = 8200$)] could be converted partially into its *diastereomer* **8** [b.p.: 75°/0.05 Torr; $m/e = 206$; IR. (CCl_4): 1730, 1635 cm^{-1}; NMR. (CCl_4): $\delta = 1.14$ (*s*, 3); 1.27 (*s*, 3); 1.70 ($d \times d$, $J_1 = 12$, $J_2 = 8.5$; 1); 1.92 ($d \times d$, $J_1 = 12$, $J_2 = 8$; 1); 1.91 (*s*, 3); 2.17 (*s*, 3); 3.27 (broadened *qua*, $J = 8.5$; 1); 3.69 (*d*, $J = 8.5$; 1); 4.77 (broadened *d*, $J = 7$; 1); 5.30 ($d \times d$, $J_1 = 7$, $J_2 = 2.5$; 1); UV. (pentane): 266.5 ($\varepsilon = 9500$)] by chromatography on basic alumina. The stereochemical assignments for **4** and **8** are based on comparisons of the experimental coupling constants of H_b *vs.* $H_{b'}$ (4.45 Hz *vs.* 8.5 Hz, see *Scheme 3*). Further structural information about **4** was obtained from its *ozonization products* **9** and **10** [**9** b.p.: 115°/0.2 Torr; $m/e = 178$ ($M^+ - 60$, CH_3COOH); IR. (CCl_4): 2750, 1758, 1735, 1690, 1637 cm^{-1}; NMR. (CCl_4): $\delta = 1.24$ (*s*, 3); 1.27 (*s*, 3); 1.8–2.2 (*m*, 2); 2.12 (*s*, 3); 2.16 (*s*, 3); 3.93 (br. *m*; 1); 5.52 (*d*, $J = 3$; 1); 5.87 ($d \times d$, $J_1 = 5$, $J_2 = 2$; 1); 9.58 (*d*, $J = 5$; 1); UV. (pentane): 235 nm ($\varepsilon = 10200$); **10**: IR. (CCl_4): 3480, 1783, 1620 cm^{-1}].

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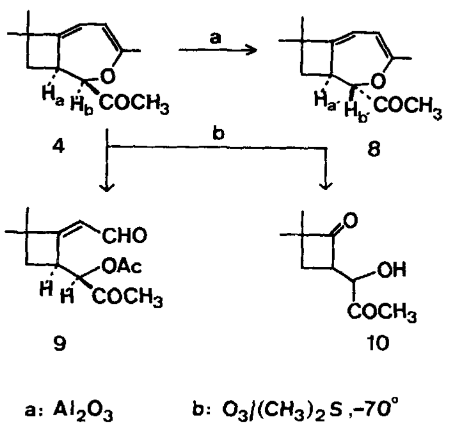
[4] The literature on oxidative cleavage of enolethers by periodic acid or periodates is somewhat meagre; for references see [3].

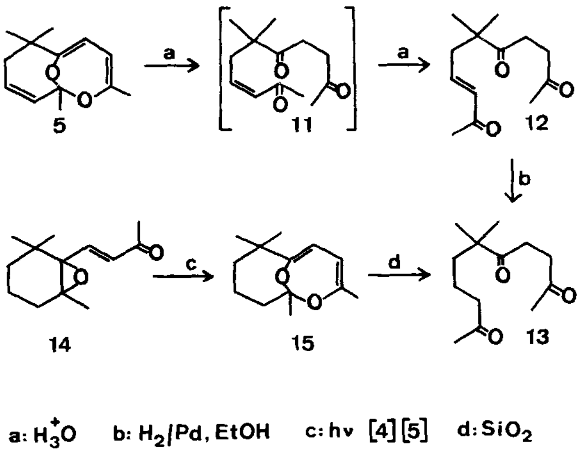
[5] The presence of the enolether function in **2** and **3** is associated with a general chemical instability of these isomers, particularly towards acids.

Scheme 3



The structure of the *ketal* **5** [b.p.: 56–60°/0.02 Torr; IR. (CCl_4): 1640 cm^{-1}; NMR. (CCl_4): $\delta = 1.06$ (*s*, 3); 1.18 (*s*, 3); 1.59 (*s*, 3); 1.64 ($d \times d \times d$, $J_1 = 12$, $J_2 = 6$, $J_3 = 2$; 1); 1.86 (*d*, $J = 1$; 3); 2.34 ($d \times d$, $J_1 = 12$, $J_2 = 4$ slightly broadened; 1); 4.51 (slightly broadened *d*, $J = 7$; 1); 5.05 (*d*, $J = 7$; 1); 5.28–5.68 (*m*, 2); UV. (pentane): 258 nm ($\varepsilon = 8200$)] was confirmed by hydrolysis with *p*-toluenesulfonic acid in moist ether to yield the aliphatic *α,β-unsaturated triketone* **12**[6]) [$C_{13}H_{20}O_3$; IR. (CCl_4): 1728, 1712, 1684, 1636 cm^{-1}; NMR. (CCl_4): $\delta = 1.20$ (*s*, 6); 2.16 (*s*, 3); 2.18 (*s*, 3); 2.39 ($d \times d$, $J_1 = 7.5$, $J_2 = 1$; 2); 2.66 (*s*, 4); 5.92 ($d \times t$, $J_1 = 16$, $J_2 = 1$; 1); 6.56 ($d \times t$, $J_1 = 16$, $J_2 = 7.5$; 1); UV. (pentane): 218.5 ($\varepsilon = 11500$)], which was finally hydrogenated to the known *triketone* **13** [4].

Scheme 4



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[6]) **12** has (*E*)-configuration (NMR.) and must be a secondary product formed by the action of acid on the undetected (*Z*)-compound **11**.

Like its isomers **2** and **3**, compound **5** could not be chromatographed on silica gel. Its dihydro derivative **15** has recently been isolated as an irradiation product of (*E*)-*β*-ionone-epoxide (**14**) [5]. *Compound* **15** is readily hydrated during chromatography on silica gel to the *triketone* **13**, thus demonstrating that the latter is not a genuine photoproduct [4].

The mechanism of these novel photoreactions has not yet been investigated. However, it seems plausible that C–C-bond cleavage of the oxirane ring in the excited species of **1** is the key step in the observed isomerization processes. Irradiation of the separate isomers **2** and **3** has shown that the reaction sequence $\mathbf{2} \rightleftarrows \mathbf{3} \rightarrow \mathbf{4} + \mathbf{5}$ is involved in the formation of the new products.

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[2] *J. A. Findley & W. D. Mac Kay*, Canad. J. Chemistry *49*, 2369 (1971).
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[4] *B. R. von Wartburg, H. R. Wolf & O. Jeger*, Helv. *56*, 1948 (1973).
[5] *B. R. von Wartburg*, to be published.

Erratum

Helv. *57*, 1974 (1974), mémoire N° 214 par *F. Cocu & al.*: p. 1981, 4e ligne à partir du haut, remplacer 3 par 5 (= 4′); p. 1981, 5e ligne à partir du haut, remplacer 145° par 150°.

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i.b./c.c. Symposium

'Future developments for additives, chemicals, fillers and renforcements for resins, molding compounds, foamed plastics, film, sheeting, profiles laminates and synthetic resing coating'.

Strombeek (Belgium), March 19–20, 1975

Further informations: i.b./c.c. Administration, Nieuwelaan 65, B–1820 Strombeek (Belgium).

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'Technical and economic evaluation – markets and future trends for organic and inorganic intermediate chemicals, drugs, fine chemicals and active principles'.

Strombeek (Belgium), October 22–23, 1975

Further informations: i.b./c.c. Administration, Nieuwelaan 65, B–1820 Strombeek (Belgium).