Reaction of 1-Benzoxepin with Singlet Oxygen: a Novel Endoperoxide

By Jack E. Baldwin* and O. William Lever, jun.
(*Chemistry Department, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139)

Summary Singlet ($^1\Delta g$) oxygen reacts with 1-benzoxepin by 2,5-addition to yield a novel endoperoxide, 2,5-epidioxy-1-benzoxepin, which undergoes an unusual rearrangement on deoxidation with trimethyl phosphite.

Several recent reports have described the reaction of the tautomeric benzene oxide–oxepin system (**1**) $\rightleftharpoons$ (**2**) with singlet oxygen.[1–3] The benzene oxide form (**2**) apparently reacts to yield the peroxy-epoxide (**3**). We report here the first isolation of an endoperoxide of an oxepin derivative.

Photosensitized oxygenation (CH_2Cl_2; Methylene Blue; 20°) of 1-benzoxepin (**4**)[4] provided the endoperoxide (**5**) in yields up to 60%, m.p. 62—63°; $\lambda_{max.}$ (Et_2O), 285 (ϵ 1530), 278 (1675), and 212 nm (7230); δ ($CDCl_3$) 5·15 (2 × dd, 1H, *J* 1·5, 1·5, and 7 Hz), 6·17 (m, 2H), and 6·67—7·50 (m, 5H); *M* 176 (mass spec.)† In the benzoxepin system (**4**) it is established that the valence tautomer, the naphthalene oxide (**6**), does not contribute to the ground state to any major extent (<5%)[5] and so the endoperoxide from (**4**) was the only product.

Deoxygenation of (**5**) with trimethyl phosphite proceeded cleanly to the aldehyde (**7**), ν_{max} 1730 cm^{-1}. This unstable

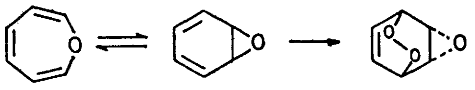
---

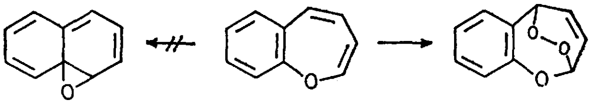
† All new compounds have given satisfactory analytical data.

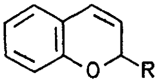
compound was best isolated as the alcohol (**8**), $\lambda_{max.}$ (EtOH), 309 (ϵ 3550) and 267 nm (4720), obtained by reduction with sodium borohydride.[6] The most economic mechanistic possibility for the conversion of (**5**) into (**7**) involves the formation of the zwitterion (**9**) by attack of phosphite on the peroxide bridge, followed by loss of phosphate to the quinone methide (**10**) and subsequent cyclisation.[7] This path is in sharp contrast to the decomposition of ascaridole with phosphines,[8] and is a consequence of the presence of the oxepinoid ring system. Finally, the endoperoxide (**5**) is stable for prolonged periods at 80° (100 h), unlike the benzene oxide endoperoxide (**3**) which is converted into a benzene trioxide at 45°.[1,2]

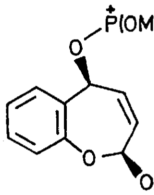
We thank Eli Lilly & Co. for support.

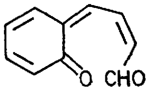
(*Received*, 12*th March* 1973; *Com.* 329.)


(1) (2) (3)


(6) (4) (5)


(7) R = CHO
(8) R = CH_2OH


(9)


(10)

---

[1] C. H. Foster and G. A. Berchtold, *J. Amer. Chem. Soc.*, 1972, **94**, 7939.

[2] E. Vogel, H.-J. Altenbach, and C.-D. Sommerfeld, *Angew. Chem. Internat. Edn.*, 1972, **11**, 939.

[3] C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Amer. Chem. Soc.*, 1973, **95**, 586.

[4] (a) E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem. Internat. Edn.*, 1964, **3**, 642; (b) F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, 1964, **86**, 3168.

[6] The parent 3-chromen has $\lambda_{max.}$ 307 (ϵ 3090) and 264 nm (4365), *cf.* I. Iwai and J. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1042.

[7] Recent examples of this cyclisation have been reported; E. E. Schweizer, T. Minami, and D. M. Crouse, *J. Org. Chem.*, 1971, **36**, 4028; R. Hug, Gy. Frater, H.-J. Hausen, and H. Schmid, *Helv. Chim. Acta*, 1971, **54**, 306.

[8] G. O. Pierson and O. A. Runquist, *J. Org. Chem.*, 1969, **34**, 3654.