Tetrahedron Letters No. 10, pp 803 - 806, 1975. Pergamon Press. Printed in Great Britain.

PHOTO-INDUCED REARRANGEMENTS OF α,β-EPOXY DIAZOMETHYL KETONES

P.M.M. van Haard, L. Thijs and B. Zwanenburg*
Department of Organic Chemistry, University of Nijmegen,
Toernooiveld, Nijmegen, The Netherlands

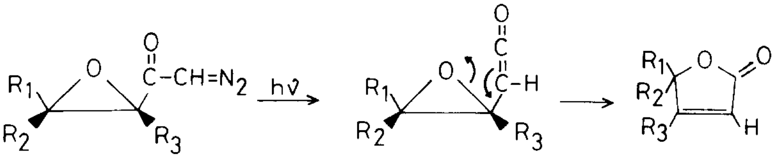
(Received in UK 30 December 1974; accepted for publication 31 January 1975)

Recently[1] we described the preparation of a new class of compounds, containing two reactive functional groups, *viz.* α,β-epoxy diazomethyl ketones (I). This paper deals with the question as to whether a Wolff rearrangement of the diazomethyl ketone moiety to a ketene group can be accomplished with leaving the epoxide function intact and thus providing a route to the interesting, yet unknown, epoxyketenes II.

Irradiation[2] of the β,β-diphenyl α,β-epoxy diazomethyl ketone Ia in benzene solution afforded, after the evolution of nitrogen had ceased (1.5-2 h) a single compound to which the butenolide structure IIIa (see Chart I) was attributed on the basis of the following evidence. The product (m.p. 131-131.5°, lit.[3] 131.6-132.2°) showed characteristic[4] infrared bands (CCl_4) at 1770, 1740-1700 ($\nu_{C=O}$) and 1665 ($\nu_{C=C}$) cm^{-1}, and NMR ($CDCl_3$) absorptions at δ 7.3 (m, 10 H, C_6H_5) and at δ 6.07 + 7.72 ppm (AB qu, 2H, J 5 Hz).

CHART I

Photolysis of α,β-epoxy diazomethyl ketones in benzene



I II III

	R_1	R_2	R_3	yield
Ia:	C_6H_5	C_6H_5	H	IIIa: 90%
Ib:	H	C_6H_5	H	IIIb: 90%
Ic:	H	C_6H_5	C_6H_5	IIIc: 70%
Id:	CH_3	CH_3	H	IIId: 43%

Similarly, the epoxy diazomethyl ketone Ib resulted in the butenolide IIIb (oil[5]; IR (CCl_4), 1785, 1760 and 1655 cm^{-1}; NMR (CCl_4), δ 7.3 (m, 5H, C_6H_5), 7.48 (d of d, 1H, H_4), 6.15 (d of d, 1H, H_3), 5.95 ppm (d of d, 1H, H_5), $J_{3,4}$ 5.5, $J_{3,5}$ 2.4, $J_{4,5}$ 2.0 Hz). Compound Ic gave the product IIIc (m.p. 149-151°, lit.[6] 147.5-150°; IR (CCl_4), 1760, 1620 cm^{-1}; NMR ($CDCl_3$), δ 7.3 (m, 10 H, C_6H_5), 6.30 and 6.52 ppm (both d, 1H, J 1 Hz); UV (EtOH), λ_{max} 217, 272 nm. The butenolide IIId was obtained by irradiation of Id (IR and NMR spectra identical with those reported in lit.[7]).

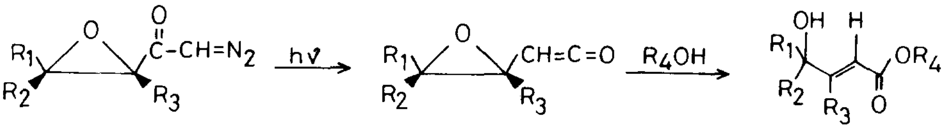
To explain the formation of the butenolides we suggest that the epoxyketenes II, which are initially formed by a Wolff rearrangement[8], undergo an intramolecular cyclization reaction as indicated in Chart I. Support for the intermediacy of the epoxyketenes II was obtained by conducting the irradiation of Ic in a matrix in methylcyclohexane at -176°. During the irradiation the intensity of the sharp and single band of the diazo group at 2130 cm^{-1} in the low-temperature IR spectrum slowly decreased. After some time a distinct new band, attributable to the ketene function, appeared at 2140 cm^{-1}, which vanished by raising the temperature of the reaction mixture.

Thermolysis of the epoxy diazomethyl ketone Ic in refluxing pentachloro ethane for 20 min (then the diazo peak in the IR had disappeared) resulted also in the formation of the butenolide IIIc (yield 30%, after chromatography on Florisil). Adamantane-spiro-2-oxiranyl diazomethyl ketone gave upon thermolysis in boiling pentachloro-ethane for 35 min the corresponding adamantane spiro-butenolide (yield 56%, after chromatography on Florisil, m.p. 122°; IR (KBr), 1740-1730, 1645 cm^{-1}; NMR (CCl_4) two d at δ 5.90 and 7.70 ppm, J 5.5 Hz).

Irradiation of the epoxy diazomethyl ketones in benzene solutions containing a ten-fold molar excess of either methanol or ethanol, resulted in quite different products, *viz.* γ-hydroxy α,β-unsaturated esters[14] (Chart II).

CHART II

Photolysis of α,β-epoxy diazomethyl ketones in benzene/methanol



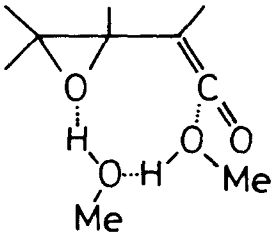
I II IV(R4=Me),V(R4=Et)

Ia	IVa	R_4 = Me	(80%)	R_4 = Et (80%)
Ib	IVb	"	(90%)	
Ic	IVc	"	(95%)	
Id	IVd	"	(80%)	R_4 = Et (57%)

The products IV and V were characterized by means of their spectral features (IVa, m.p. 96-97^o; IR (KBr), 3455, 1700, 1630, 990 cm^{-1}; NMR ($CDCl_3$), δ 7.43 (d, 1H, H_β, $J_{\alpha\beta}$ 16 Hz), 6.08 (d, 1H, H_α, $J_{\alpha\beta}$ 16 Hz), 3.50 (s, 3H, CH_3) and 2.85 ppm (s, 1H, O*H*, exchanges with D_2O), UV (EtOH), λ_{max} 225 nm; Va, oil, NMR, instead of the CH_3 signal the qu and tr for the C_2H_5 group; IVb, oil; IR (CCl_4), 3450 (br), 1720, 1650, 980 cm^{-1}; NMR (CCl_4), δ 6.92, 5.98 and 5.16 (all d of d, 1H, H_β, H_α, H_γ, $J_{\alpha\beta}$ 17 Hz, $J_{\alpha\gamma}$ 1 Hz, $J_{\beta\gamma}$ 4 Hz), 3.57 (s, 3H, CH_3), 3.24 ppm (s, 1H, O*H*); IVc, oil; IR (CCl_4), 3450, 1730, 1650 cm^{-1}; NMR ($CDCl_3$), δ 6.38 (d, 1H, H_α, J 1 Hz), 5.32 (d, 1H, H_γ, J 1 Hz), 3.50 (s, 1H, O*H*), 3.38 ppm (s, 3H, CH_3); IVd, oil; IR (CCl_4), 3450, 1730, 1665 cm^{-1}; NMR ($CDCl_3$), 6.93 (d, 1H, H_β, J 16 Hz), 5.93 (d, 1H, H_α, J 16 Hz), 3.66 (s, 3H, OCH_3) and 1.30 ppm (s, 6H, CH_3); the spectra of Vd were identical with those given in lit.[7]). The coupling constants $J_{\alpha\beta}$ clearly show that *trans*-crotonates are obtained.

When the Wolff rearrangement of the diazomethyl ketones I was performed using silver benzoate/triethylamine in methanol the same γ-hydroxy crotonates were obtained. However, in this case the products were difficult to purify and only obtained in moderate yields.

In order to rationalize the reaction products formed during the photolysis in the presence of an alcohol again the epoxyketenes II are proposed as the primary intermediates. Three possible routes can now be envisaged to explain the formation of the γ-hydroxy crotonic esters: *i*. cyclization of II to the butenolides III (see Chart I) followed by alcoholysis, *ii*. formation of β,γ-epoxy esters by an initial reaction of the ketene group with alcohol and subsequent epoxide opening *via* enolization of these esters (*cf*. the reaction of β,γ-epoxy ketones[9]), *iii*. concomitant epoxide opening during the nucleophilic reaction of the alcohol with the ketene function. The first possibility can be ruled out since the butenolides III do not react[10] with methanol under the chosen conditions as was shown in blank experiments. Judging from the rather strong basic and acidic conditions[11] required for the conversion of some known β,γ-epoxy esters into γ-hydroxy crotonates, the intermediacy of such β,γ-epoxy esters seems not very likely under the employed, essentially neutral[12], conditions. Therefore, we consider the third possibility as the most probable mode of product formation. As convincingly shown by Lillford and Satchell[13] the spontaneous alcoholysis of ketenes proceeds *via* a cyclic transition state involving an associated alcohol species. On basis hereof, we tentatively suggest that the observed products are formed *via* a mechanism involving at least two alcohol molecules in a cyclic transition state such as presented in the figure, in which one alcohol acts as



a nucleophile on the ketene carbonyl carbon atom and the other one serves as proton source for the epoxide opening.

In conclusion, irradiation of α,β-epoxy diazomethyl ketones provides a new simple route to butenolides and γ-hydroxy α,β-unsaturated esters through the intermediacy of epoxyketenes.

References and Notes

1. B. Zwanenburg and L. Thijs, Tetrahedron Lett., 1974, 2459.
2. The irradiations were conducted using an internal water-cooled 700 W Hanovia medium pressure mercury lamp (Q 700) with a Pyrex filter. The concentration of the substrate was about 500 mg/l.
3. M.S. Newman, L.M. Joshel and P.H. Wise, J. Amer. Chem. Soc. 62, 1861 (1940).
4. Y.S. Rao, Chem. Rev. 64, 353 (1964).
5. J. Thiele and N. Sulzberger, Lieb. Ann. Chem. 319, 196 (1901).
6. P. Yates and J.A. Weisbach, J. Amer. Chem. Soc. 85, 2943 (1963).
7. G. Buchi and S.H. Feairheller, J. Org. Chem. 34, 609 (1969).
8. W. Kirmse, Carbene Chemistry, 2nd Ed. Academic Press, 1971, p. 475.
9. A. Padwa, D. Crumrine, R. Hartman and R. Layton, J. Amer. Chem. Soc. 89, 4435 (1967).
10. *Cf.* ref. 4, p. 370.
11. R. Rambaud and S. Ducher, Bull. Soc. Chim. France, 1956, 466; R. Rambaud, S. Ducher, A. Broche, M. Brini-Fritz and M. Vessiere, *ibid* 1955, 877; W.W. Epstein and A.C. Sonntag, Tetrahedron Lett. 1966, 791.
12. Prior to use the photolysis apparatus was thoroughly cleansed, rinsed with dilute ammonia and water and then dried.
13. P.J. Lillford and D.P.N. Satchell, J. Chem. Soc. B, 1968, 889.
14. Note added during the typing of the manuscript: Very recently N.F. Woolsey and M.H. Khalil, Tetrahedron Lett. 1974, 4309, described the formation of IVb by photolysis of Ib in methanol.