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THERMAL AND PHOTO DECOMPOSITION OF AN EXPOXYDIAZO KETONE; DIVERGENT REACTIONS

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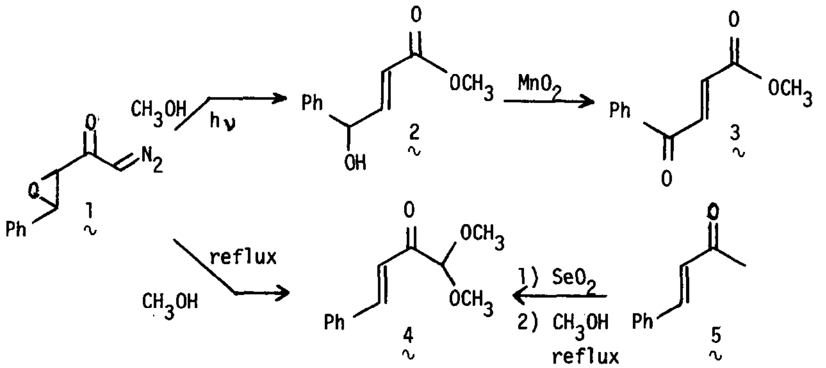
As part of our continuing efforts to extend the synthetic utility of diazo ketones,[1] we have examined the photochemical and thermal reactions of 1-diazo-3,4-epoxy-4-phenyl-2-butanone (1) which has recently become readily available.[1b,2]

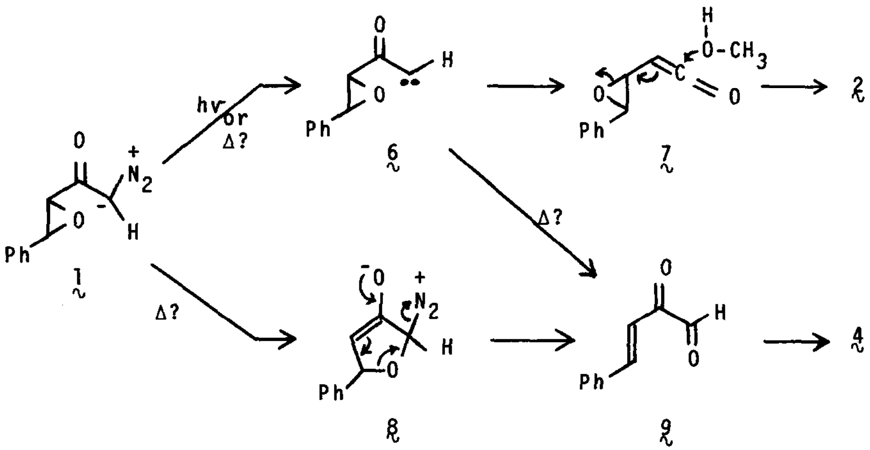
Irradiation of 1 in methanol solution (λ>300 nm) gave methyl 4-hydroxy-4-phenyl-2-butenoate (2)[3] in 62% yield as an unstable brown oil which was isolated by chromatography on Florisil, ir (neat) 2.88 (w, OH), 5.82 (s, COOR), 6.04μ (s,C=C); nmr (CCl_4) δ 7.82(s, 5 H, Ph), 6.92 (q, 1 H, CH=C$\underline{H}$CHOH, J=16 Hz, J' = 5 Hz), 6.00(q,1H, C$\underline{H}$=CHCHOH, J=16Hz, J"= 2Hz), 5.15 (q, 1 H, CH=CHC$\underline{H}$OH, J'=5 Hz, J''=2 Hz), 3.65 (s, 3 H OCH_3) and 3.12 ppm (s, 1 H, OH). The assigned structure 2 was confirmed by conversion to the known[4] keto ester 3 in 74% by activated manganese dioxide oxidation, mp 28.5-29.5.°

In contrast, refluxing 1 in methanol for 48 hr gave, after chromatography on alumina (activity II), 1,1-dimethoxy-4-phenyl-3-buten-2-one (4)[3] in 75% yield, bp (capillary) 248-250°, n_D^{27}1.5640; ir (neat) 5.97(s,C=O), 6.17μ(s, C=C); nmr (CCl_4) δ 7.70 (d, 1 H, J=16 Hz, vinylic), 7.42 (m, 5 H, Ph), 6.98 (d,



1 H, J=16 Hz, vinylic), 4.50 (s, 1 H, $C\underline{H}OCH_3$), 3.38 ppm (s, 6 H, OCH_3). This compound was synthesized from 4-phenyl-3-buten-2-one (**5**) by selenium dioxide oxidation[5] followed by refluxing the resulting keto aldehyde **9** in methanol.

Mechanistically, irradiation of **1** could lead to the epoxy ketene **7** *via* Wolff rearrangement of the expected keto carbene **6**. Nucleophilic attack of methanol with concomitant ring opening would result in formation of **2**. Although direct intramolecular oxygen abstraction[6] from a thermally generated carbene **6** could form unsaturated keto aldehyde **9** and thus **4**, a more ready rationalization of the divergent reaction paths involves formation of **8** from **1** before nitrogen loss[7]. Loss of nitrogen from **8**, concerted with ring cleavage would then form **9**. A more detailed discussion of the mechanistic possibilities will appear in our full paper.



1. a) N. F. Woolsey and M. H. Khalil, *J. Org. Chem.*, **37**, 2405 (1972); b) *ibid.*, **38**, 4216 (1973).

2. **1** has more recently become available by another route, B. Zwanenburg and L. Thijs, *Tetrahedron Lett.*, 1974, 2459.

3. All new compounds gave satisfactory analytical data.

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6. H. Nozaki, H. Takaya and R. Noyori, *Tetrahedron*, **22**, 3393 (1966).

7. We thank a referee for suggesting this possibility.