## DEOXYGENATION OF EPOXIDES BY FLUORENYLIDENE

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**Summary:** Irradiation of 9-diazofluorene in the presence of epoxides yields fluorenone and an equimolar concentration of the alkene formed from the stereospecific deoxygenation of the epoxide.

It is well known that electrophilic singlet carbenes often react by direct attack on a bonding or non-bonding electron pair in the reagent molecule.<sup>1</sup> This process is believed to initiate the insertion into carbon-hydrogen bonds of hydrocarbons,<sup>2</sup> stereospecific formation of cyclopropanes from olefins,<sup>3</sup> oxidative addition to alcohols,<sup>4</sup> and the formation of ylide intermediates from reagents containing heteroatomic functional groups.<sup>5</sup> This last process forms the central part of a remarkable series of reactions reported recently by Kirmse and coworkers<sup>6</sup> in which methylene (:CH<sub>2</sub>) was shown to react with cyclic ethers to give products characteristic of a Stevens rearrangement and of  $\beta$ -elimination. In this report we describe the photolysis of 9-diazofluorene (DAF) in the presence of epoxides. Our observations indicate that fluorenylidene<sup>7</sup> [FL] reacts with epoxides through an ylide which rearranges to give 9-fluorenone (FLO) and the alkene derived from deoxygenation of the epoxide, eq 1.



Irradiation of DAF (5 x  $10^{-3}$  M, 350 nm) in degassed, neat <u>cis</u>-2,3-epoxybutane gives FLO (60%) and an equivalent amount of 2-butene. In addition, this reaction produces 9,9'-bifluorenyl (23%) and two low yield adducts of the carbene to the epoxide (1 and 2). Adducts 1 and 2 were isolated from the photolysis mixture by preparative gas chromatography. Compound 2 was identified by independent synthesis of an authentic sample; 1 is converted to 2 by treatment with acid.<sup>8</sup> Similar results are obtained from the irradiation of DAF in trans-epoxybutane, styrene oxide, and cyclohexene oxide. In these cases the yield of FLO is 50, 50 and 30% respectively. In contrast, irradiation of diphenyldiazomethane in degassed, neat cis-epoxybutane gives only a very low yield of benzophenone (<7%). Deoxygenation of epoxides by metallo-carbenes has been reported previously.<sup>9</sup>



Since triplet carbones react very rapidly with molecular oxygen to form ketones,<sup>10</sup> we carefully eliminated the possibility that the FLO obtained in these reactions is formed by this path. Photolysis of solutions of DAF in acetonitrile degassed by repetitive freeze-pump-thaw cycles  $(10^{-6} \text{ mm})$  gave no FLO (<2%) if they did not also contain an epoxide (30% v/v <u>cis</u>-epoxybutane gives 51% FLO).

The olefins formed from deoxygenation of epoxides by photolysis of DAF retain the stereochemistry of the epoxide. Irradiation of the diazo compound in neat <u>cis-2,3-epoxybutane</u> gives only <u>cis-2-butene</u> (>93% retention of configuaration by the limit of detectability of the trans isomer in the photolysis mixture). Similarly, only <u>trans-2-butene</u> is formed from irradiation of DAF in <u>trans-2,3-epoxybutane</u> (>95% stereoselectivity can be demonstrated in this case).

The relative rate of alkene formation from reaction of FL with the <u>cis</u>- and <u>trans</u>-epoxybutanes was obtained from analysis of competition reactions in which the ratio of the <u>cis</u>- and <u>trans</u>-2-butenes produced was determined. Photolysis of DAF in a 1:1 mixture of the isomeric epoxybutanes gives a 3.3 : 1 mixture of <u>cis</u>- to <u>trans</u>-butene. This result indicates that the reaction to form the olefin from the cis epoxide occurs ca. three times faster than with the trans isomer.

Irradiation of DAF in neat <u>cis</u>-epoxybutane with the output of a  $N_2$  laser (337 nm, 13 ns, 7 mJ)<sup>11</sup> generates a transient intermediate with an absorbtion maximum at ca. 490 nm. This species is assigned to the 9-fluorenyl radical by comparison with the reported spectrum<sup>7</sup> of this radical. Formation of the fluorenyl radical by hydrogen atom abstraction competes with the deoxygenation of the epoxide and leads eventually to the 9,9'-bifluorenyl isolated from this reaction. No other intermediates were sufficiently long-lived or absorbed strongly enough to permit detection in this laser spectroscopy experiment.

It is well-known that laser irradiation of DAF in  $CH_3CN$  generates a transient nitrile ylide that is strongly absorbing at 400 nm.<sup>7</sup> This reaction occurs with a bimolecular rate constant equal to 2.1 x  $10^6$  M<sup>-1</sup> s<sup>-1</sup> at room temperature. We find that formation of the acetonitrile ylide is inhibited by the epoxybutanes. Irradiation of acetonitrile solutions of DAF containing increasing amounts of either epoxide isomer gives progressively less of the nitrile ylide. These data, when analyzed with the usual Stern-Volmer equation,<sup>7</sup> yield straight lines with slopes of 23 and 7.6 M<sup>-1</sup> for the <u>cis-</u> and <u>trans-</u>epoxide isomers respectively. Thus, both epoxides are more effective traps of FL than is acetonitrile. Also, the cis isomer reacts with the carbene ca. three times faster than does the trans. However, the epoxides are much less effective traps of the carbene than is methyl alcohol.<sup>7</sup>

The ground state of FL has triplet spin multiplicity.<sup>7</sup> Despite this fact, under most experimental conditions a significant fraction of the bimolecular reactions of this carbene originate from its electrophilic singlet state. The energy of the singlet is only ca. 2

kcal/mol above the ground triplet state, and the two spin states equilibrate rapidly.<sup>7</sup> We propose that the deoxygenation of epoxides by reaction with FL originates with the singlet state of the carbene. This suggestion is consistent with the previously reported high electrophilicity of <sup>1</sup>(FL), the readiness with which this carbene forms ylides with other heteroatomic functional groups,<sup>5</sup> the highly stereoselective nature of olefin formation, and with the relatively low efficiency of the bimolecular trapping of the carbene by the epoxides (permitting equilibrium of the carbene spin states to be established at all epoxide concentrations).

These findings lead naturally to postulation of an oxonium ylide (3, Scheme 1) in this epoxide deoxygenation reaction. Unfortunately, we are not able to detect this species directly by transient absorption spectroscopy. This is probably a consequence of its low "steady-state" concentration owing to the relatively slow rate for its formation and a suspected rapid subsequent reaction. Formation of ylide 3 is consistent with the higher reactivity of the <u>cis</u>-epoxide isomer. The non-bonding electrons of the trans isomer are shielded sterically by the methyl groups. Also, the highly stereoselective nature of the deoxygenation reaction is consistent with concerted rearrangement of such an ylide. Additional support for the involvement of this ylide comes from analogy to the work of Kirmse<sup>6</sup> where a related species is implicated by the products obtained.



It is significant that diphenylmethylene (DPM) does not efficiently deoxygenate epoxides. The energy gap separating the ground triplet state from the excited singlet of DPM is more than twice as large as it is in FL.<sup>12</sup> This means that there is far less of singlet state DPM in equilibrium with its triplet than in the case of FL. Also, it is anticipated from the simplest sort of molecular orbital analysis that <sup>1</sup>(FL) will be more electrophilic than <sup>1</sup>(DPM).<sup>13</sup> Thus we conclude that the difference in epoxide deoxygenation ability between DPM and FL is a consequence of slow ylide formation in the former.

In sum, our findings reveal a potentially general reaction of electrophilic singlet carbenes. The deoxygenation of epoxides seems to proceed through an oxonium ylide which rearranges rapidly to give a carbonyl compound and an olefin with retained stereochemistry. Facile epoxide deoxygenation is a sought-after synthetic process.<sup>9</sup> These results should guide the search toward carbenes which could be useful in this regard.

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- 8. 1: <sup>1</sup>H NMR ( $C_{6}D_{6}$ ) 6.8-7.7 (m), 3.5 (s, 1H), 2.9 (q, 1H), 1.0 (d, 3H), 0.55 (s, 3H). M<sup>+</sup> 236. 2: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.2-7.8 (m, 8H), 4.5 (d, 1H), 3.25 (2 x q, 1H), 2.25 (s, 3H), 0.65 (d, 3H). M<sup>+</sup> 236.
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