

## PHOTOSENSITIZED OXYGENATION OF 3-DIAZOCAMPHOR<sup>1</sup>

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**Summary:** Photosensitized oxygenation of 3-diazocamphor gave camphorquinone and camphoric anhydride in benzene. The yield of camphoric anhydride did not depend on the concentration of added camphorquinone or of diazocamphor. When the reaction was carried out in acetonitrile or benzonitrile, amide 7 or 8 was produced. The formation of amide strongly supports the intermediacy of a carbonyl oxide.

During past forty years the reaction mechanism for abnormal ozonolysis of  $\alpha,\beta$ -unsaturated carbonyl compounds, which involves the cleavage not of the olefinic double bond but of the carbon-carbon single bond between the double bond and the carbonyl group, to give an acid anhydride or acid, has not been well known. Many mechanisms have been proposed, including rearrangement of ozonide<sup>2</sup>, decomposition of hydrated ozonide<sup>3</sup>, and oxydation of produced  $\alpha$ -dicarbonyl compound<sup>4</sup>. As one of these mechanisms, Criegee and his co-workers<sup>5</sup> proposed that  $\alpha$ -carbonyl carbonyl oxides are key intermediates on the abnormal ozonolysis of  $\alpha,\beta$ -unsaturated carbonyl compounds. Similarly the intermediacy of  $\alpha$ -carbonyl carbonyl oxides was proposed for ozonation of alkynes<sup>6</sup>, where the intermediate was considered to be converted to an acid anhydride, too.

We now report that an  $\alpha$ -carbonyl carbonyl oxide produced from the reaction of an  $\alpha$ -diazoketone with singlet oxygen rearranges to an acid anhydride. Two typical  $\alpha$ -diazoketones, one aliphatic, the other aromatic, namely, 3-diazocamphor (1) and 7-diazo-8-acenaphtenone (2), were chosen as model compounds. When a benzene or dichloromethane solution of 1 or 2 was photooxidized with a 55x6-W Na-lamp for 1 hr in the presence of meso-tetraphenyl porphine (TPP) or methylene-blue as a sensitizer, a 1,2-diketone, camphorquinone (3) or acenaphtenequinone (5), and an acid anhydride, camphoric anhydride (4) or naphthalic anhydride (6) were produced in the yields shown in Table I. Diketone 3 or 5 is stable under the conditions and was quantitatively recovered.

To clarify the mechanism, diketone 3 was added to a solution of diazocamphor (1) before photooxidation (Table I). It is clear that anhydride is not produced from diketone by oxygen atom transfer<sup>7</sup>, because added diketone does not change the yield of anhydride. The fact that the product ratio is independent of the concentration of diazocamphor also suggests that the reaction is intramolecular (Table I). The intermediate was successfully trapped in the nitrile solvent, acetonitrile and benzonitrile, to give amide 7 (mp 64-65°C,  $\nu_{\text{max}}^{\text{cm}^{-1}}$  1690, 1730, 1790) and 8 (mp 118-119°C,  $\nu_{\text{max}}^{\text{cm}^{-1}}$  1675, 1720, 1790) in 5 and 12 % yield, respectively, along with camphorquinone and camphoric anhydride. Although there are no previous reports of the trapping of a carbonyl oxide by a nitrile, the formation of amide 7 or 8 strongly supports the intermediacy of carbonyl oxide 9.

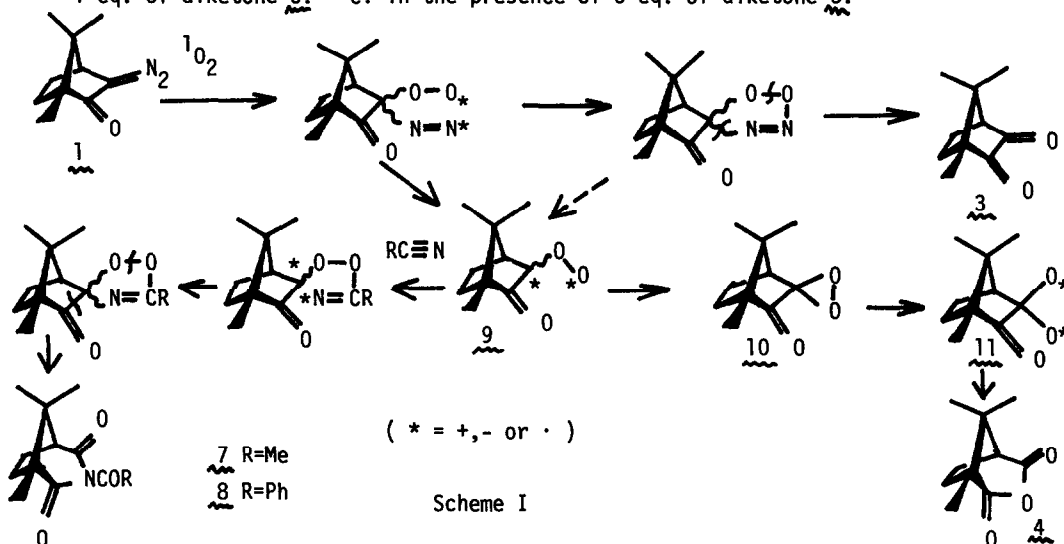
We propose the reaction mechanism shown in Scheme I. The rearrangement of dioxirane 10 to acid anhydride<sup>8</sup> can proceed via singlet diradical 11<sup>9</sup> without interception by triplet oxygen. Ionic intermediate would correspond to excited state of diradical 11<sup>9</sup>. A conceivable concerted

path is unfavourable, because concerted breaking of two bonds would need a high activation energy<sup>10</sup>.

Table I. Products yields in photooxygenation of 1 and 2.

|           | <u>1</u>          |                                      |                     |                     | <u>2</u>               |                        |                   |                                      |
|-----------|-------------------|--------------------------------------|---------------------|---------------------|------------------------|------------------------|-------------------|--------------------------------------|
|           | Bz-TPP            | CH <sub>2</sub> Cl <sub>2</sub> -M.B | Bz-TPP <sup>b</sup> | Bz-TPP <sup>c</sup> | Bz-TPP                 | Bz-TPP                 | Bz-TPP            | CH <sub>2</sub> Cl <sub>2</sub> -M.B |
|           | 5.21 <sup>a</sup> | 7.82 <sup>a</sup>                    | 5.21 <sup>a</sup>   | 5.21 <sup>a</sup>   | 8.06x10 <sup>-1a</sup> | 4.03x10 <sup>-2a</sup> | 8.11 <sup>a</sup> | 6.12 <sup>a</sup>                    |
| Diketone  | 51 %              | 61 %                                 | -                   | -                   | 53 %                   | 54 %                   | 42 %              | 46 %                                 |
| Anhydride | 24 %              | 38 %                                 | 29 %                | 29 %                | 32 %                   | 26 %                   | 44 %              | 51 %                                 |

Yields were determined by G.L.C. a: [1]x10<sup>3</sup>M or [2]x10<sup>3</sup>M b: in the presence of 1 eq. of diketone 3. c: in the presence of 5 eq. of diketone 3.



#### References

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