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TRIOXABICYCLO [2,1,0] PENTANE IH PHOTOSENSITIZED OXYGENATION OF 2-DIAZO-3-BUTANONE

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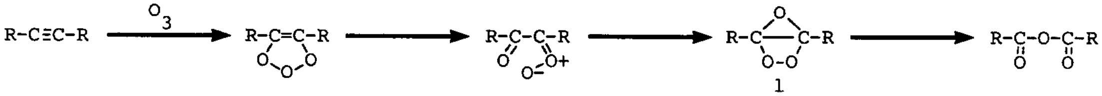
Summary: Photosensitized oxygenation of 2-diazo-3-butanone at -78°C in CH_2Cl_2 gave trioxabicyclo [2,1,0] pentane which has a long enough life time to allow chemical and spectroscopic characterization.

Despite extensive investigation of 1,2-dioxetanes, in photosensitized oxygenation of olefin, the four membered ring peroxide containing linkage to a small heterocyclic ring remain hypothetical intermediates. These compounds may possess inherent interest because of their high energy content and may be important intermediates in chemiluminescent systems. Recently, chemienergized benzoic anhydride has been claimed in the low temperature ozonation of diphenyl acetylene and the trioxabicyclo [2,1,0] pentane (1) has been assumed to be a precursor of anhydride.1) Such a dioxetane (1) probably arises from the intramolecular cyclization of carbonyl oxide to the adjacent ketone. Carbonyl oxide has been reported in the photosensitized oxygenation of diazo compounds;2) the α-carbonyl carbonyl oxide especially shows strong oxenoid character.3) We now report some evidence for the dioxetane (1) from rearrangement of an α-carbonyl carbonyl oxide in the low temperature photooxygenation of 2-diazo-3-butanone (2), the first example of the direct observation of the intermediate.



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2-Diazo-3-butanone (2) (0.4 mmol) in CH_2Cl_2 was oxygenated at -78°C with TPP as a sensitizer using a xenon lamp through a UV cut off filter and the reaction mixture was warmed to room temperature, resulting in the formation of biacetyl (55 %), acetic anhydride (27 %) and acetic acid (6 %) together with N_2 (44 %) and N_2O (56 %).4) The ^1H nmr spectrum of the reaction mixture in CD_2Cl_2 at -78°C showed resonances at 2.43 ppm (methyl protons of biacetyl), 2.23 (methyl protons of acetic anhydride), and 1.56 (methyl protons of intermediate) (Figure I). The ^{13}C nmr spectrum also showed resonances of biacetyl, acetic anhydride and the intermediate at 108.3 ppm (Figure II). The resonance signals at 1.56 and 108.3 ppm gradually decreased with increasing temperature and completely disappeared at 0°C with an increase of anhydride peak. These resonance peaks at 1.56 and 108.3 ppm are well consistent with the formulation of trioxabicyclo [2,1,0] pentane.5) Because of the

Figure I

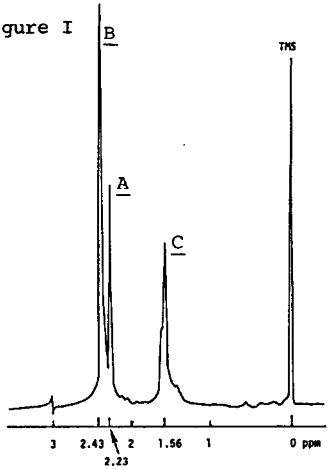
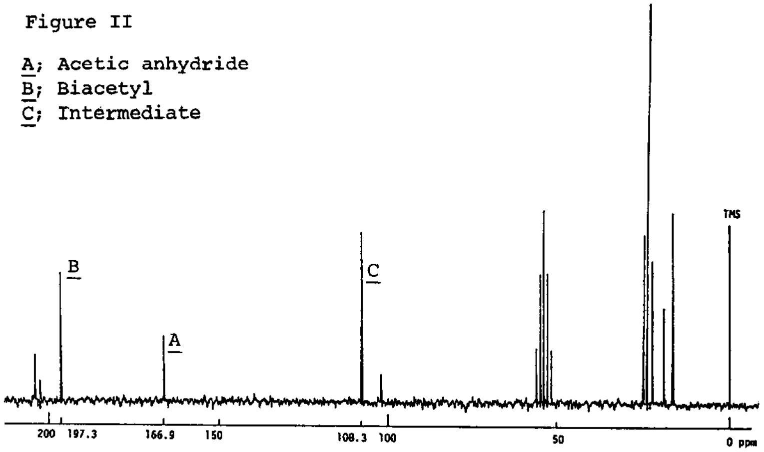


Figure II

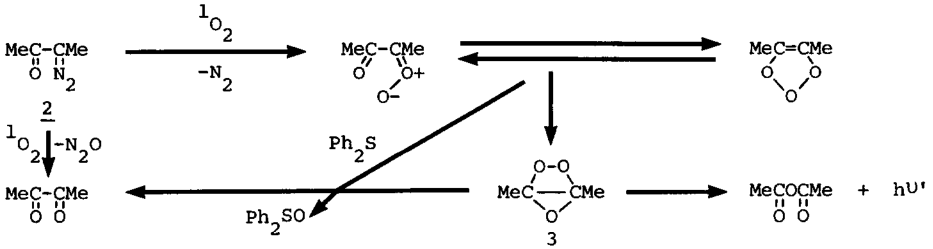


*Low temperature ^{1}H nmr and ^{13}C nmr spectrum of the reaction mixture.

exceptionally high energy content of the dioxetane (3), the temperature of the reaction vessel with an attached photomultiplier was gradually increased, and light emission was observed to be maximum at -50°C both in the presence and in the absence of 9,10-dibromoanthracene.

In ozonation reactions of 2-butyne, α-carbonyl carbonyl oxide and trioxalene were proposed to be in equilibrium and to transfer oxygen atom to substrate.[6] Investigation of the oxygen atom transfer reaction was carried out as follows. After oxygenation of 2-diazo-3-butanone at -78°C, diphenyl sulfide was added to the reaction mixture at -78°C and allowed to stand at room temperature. Biacetyl and diphenyl sulfoxide were obtained in 76 and 19 %, respectively, with 5 % of acetic anhydride. This indicates that the precursor of acetic anhydride is reducible to biacetyl, that is, the oxygen atom transferring species may be either α-carbonyl carbonyl oxide or trioxabicyclo [2,1,0] pentane (Scheme).

Scheme



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References and Notes

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4) 2-Diazo-3-butanone sometimes decomposes thermally and the yields of acetic anhydride and acetic acid are reduced.
5) The chemical shift of dioxetane ring was 109 ppm for 1,6-diphenyl-2,5,7,8-tetraoxabicyclo [4,2,0] octane. K.A.Zaklika, A.L.Thayer and A.P.Schaap, J.Am.Chem.Soc.,100,4916(1978).
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