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ACID-CATALYZED DECOMPOSITION OF AN α-KETO DIAZO ENDOPEROXIDE

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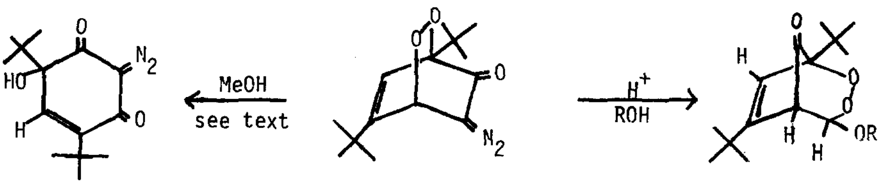
SUMMARY: Two different decomposition modes of α-keto diazo endoperoxide **1** are described. One is the Brønsted acid-catalyzed elimination of the diazo group leading to rearranged peroxides **2**. Deuterium labeling clearly shows the path of the rearrangement. The other reaction is a catalyzed cleavage of the peroxide bond to form diazoketone **3**.

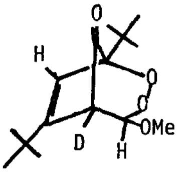
In a previous paper,[1] we showed that α-keto diazo endoperoxide (**1**), obtained in the methylene blue (MB)-sensitized photooxygenation of 4,6-di-*tert*-butyl-2-diazo-1,2-benzoquinone undergoes various photochemical and thermal reactions. We have further investigated the reactivity of **1** and found that the rearrangement of **1** to **2**, which was shown to be promoted photochemically by further irradiation of the crude MB-sensitized photooxidaiton mixture from the diazoquinone can also be catalyzed by Brønsted acids without light.

To 10-20 ml of a MeOH solution of **1**[1] was added one drop of MeOH saturated with dry HCl at r.t. After 5 min., **2a** (m.p. 111°C)[1] was obtained in quantitative yield. Spectroscopic data were identical to those previously reported for **2a**.[1] Addition of a catalytic amount of acetic acid to a MeOH solution of **1** did not cause the rearrangement. However, when **1** was dissolved in neat AcOH at r.t., reaction took place and compound **2b** was obtained as a viscous oil.[3] The NMR spectrum showed that **2b** was the sole rearrangement product.



3 1 2a: R=Me

b: R=COMe

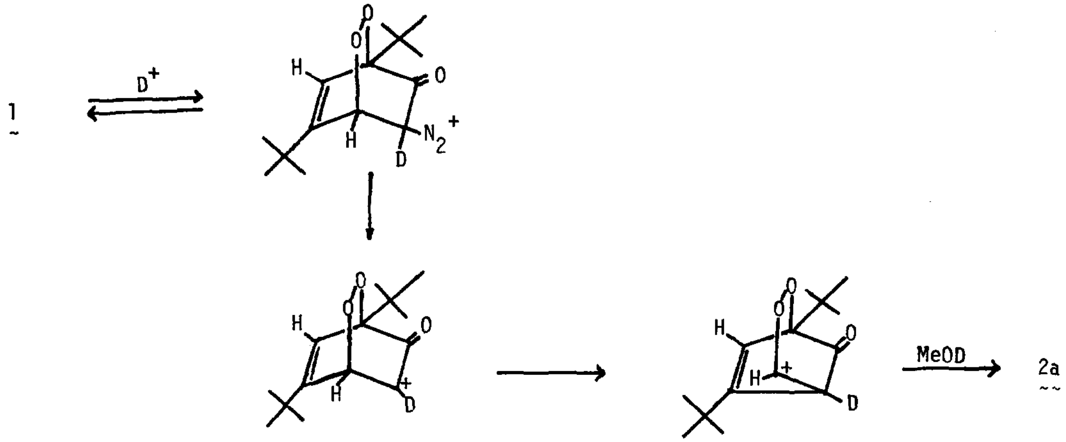


2a'

The rearrangement of 1 to 2a was examined in MeOD using dry DCl as a catalyst. After the reaction, product 2a' was analyzed by NMR. The ^{1}HNMR spectrum of 2a' showed only two methine protons at 5.06(S) and 6.09(S) with 1:1 relative ratio, whereas 2a showed three methine protons at 3.10 (d + d, J = 2.9 and 0.7 Hz), 5.06(d, J = 2.9 Hz), and 6.09 (d, J = 0.7 Hz). The results clearly show that deuterium was incorporated only at the bridgehead carbon in 2a'.

On the basis of the above result, it seems reasonable that the rearrangement from 1 to 2 proceeds via diazonium ion intermediates formed by protonation. Subsequent elimination of N$_2$ leads to the formation of carbonium ions which can rearrange as shown in Scheme I. It is remarkable that the peroxide bond survives this transformation.

Scheme I



Surprisingly, it was found that when **1** was treated overnight with MeOH which had been previously stored over molecular sieves (Linde 3a), endoperoxide bond cleavage instead of elimination of N_2 occurred and diazo-ketone **3** (yellow crystals, m.p. 80°C) was obtained.[4] The reaction proceeds slowly at r.t. and was monitored by U.V. No other products were observed. Presumably the reaction is catalyzed by metal ions or something else extracted from the molecular sieves.

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REFERNCES AND NOTES

1. H.-S. Ryang and C.S. Foote, *J. Am. Chem. Soc.* **103**, 4951 (1981). Photooxygenation of 4,6-di-*tert*-butyl-2-diazo-1,2-benzoquinone has also been reported by Ando and co-workers: W. Ando, H. Miyazaki, K. Ueno, H. Nakanishi, T. Sakurai, and K. Kobayashi, *Ibid*., **103**, 4949 (1981).
2. Photolysis of a purified sample of **1** in methanol gave a complex mixture containing some **2a**. If the crude photooxygenation mixture of the diazoquinone containing **1** (~90%) was allowed to stand for a week at r.t. in the dark, no formation of **2a** was observed. Since MB bleached under the irradiation conditions, it is probable that degradation products of MB may cause the photorearrangement, since neither pure **1** + MB + light alone nor the crude mixture in the dark gave much **2a**.
3. Compound **2b**: ^{1}HNMR δ ($CDCl_3$, 7.25 ppm) 1.10(9H,s), 1.17(9H,s), 2.17(3H,s), 2.11(1H,d, J = 3.3Hz), 6.14(1H,s), 6.40(1H,d, J = 3.3Hz); ^{13}CNMR δ ($CDCl_3$, 77.3 ppm) 25.0(q), 27.6(q), 28.3(q), 34.0(s), 54.1(d), 97.6(s), 100.5(d), 122.1(d), 160.1(s), 170.0(s), 195.5(s), ir (NaCl plate) 1760, 1720, and 1600 cm^{-1}; Mass Spectrum m/e 224(M-72), 208, 193, 180, 165, 155.
4. Compound **3**: ^{1}HNMR δ ($CDCl_3$) 0.98(9H,s), 12.8(9H), 3.32(1H,s), 6.59(1H,s); ^{13}CNMR δ ($CDCl_3$) 25.1(q), 29.5(q), 35.9(s), 41.7(s), 80.1(s), 140.9(d), 145.9(s), 179.9(s), 192.2(s); ir(KBr) 3460, 2140, 1635, 1615 cm^{-1}; Mass Spectrum m/e 208(M-56), 180, 166, 165; UV(MeOH) 274(ε = 7100) and 250 nm (ε = 9600); Anal. Found; C, 63.56; H. 7.61; N, 10.53; Calcd. for $C_{14}H_{20}N_nO_3$: C, 63.61; H, 7.64; N, 10.59.

5. For reviews on rearrangements of diazonium ions:
    a. R.A. More O'Ferrall, Adv. Phys. Org. Chem. **5**, 331 (1967).
    b. D. Whittaker in "The Chemistry of Diazonium and Diazo Groups, Part II," p. 593, ed., S. Patai, Interscience, London, 1978).
    c. For recent work on α-keto cations formed by solvolysis, see X. Creary, J. Org. Chem. **44**, 3938 (1979), J. Am. Chem. Soc. **103**, 2463 (1981), and references cited therein.

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