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A NOVEL DIOXETANE-HYDROPEROXIDE REARRANGEMENT : PHOTOOXYGENATION OF 3-TERT-BUTOXY (AND METHOXY)-6,7-BENZOBICYCLO[3.2.1]OCTA-2,6-DIENES

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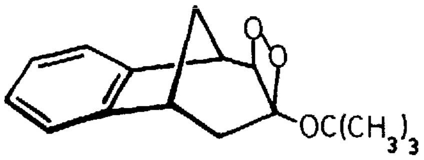
Summary: The dioxetanes 1 and 2 have been synthesized by photooxygenation of the corresponding enol ethers 5 and 6. 1 decomposed upon heating to the unexpected hydroperoxide 7 where 2 afforded the expected aldehyde-ester 12. The striking behavior of these dioxetanes has been discussed in terms of steric factors.

Despite extensive investigation of photooxygenation of conjugated and other unsaturated systems, dioxetanes remained as intermediates until 1968. Since then well over a hundred stable derivatives of dioxetanes have been isolated and characterized[1]. Most have been prepared by Kopecky's method[2], closure of the β-halohydroperoxides with base or silver salt. The classic Kopecky method of dioxetane synthesis from alkenes is the route of choice in the preparation of many simple substituted dioxetanes. Many dioxetanes have also been prepared by the addition of singlet oxygen to electron-rich olefins such as enol ethers and, enamines[1,3].

The characteristic reaction of the dioxetanes is the chemiluminescent thermal decomposition to two carbonyl fragments. Dioxetanes undergo also a number of normal peroxide reactions (metal ion catalysis, rearrangement, and reduction by insertion into the peroxide bond) in which no excited states are generated. In this reactions, dioxetanes show enhanced reactivity as compared to that of dialkyl peroxides presumably because of the strain of the ring system.

In this paper, we describe the synthesis of two new dioxetanes 1 and 2 and unusual thermal rearrangement of 1 to 7.



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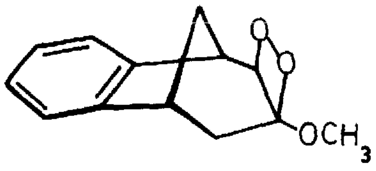

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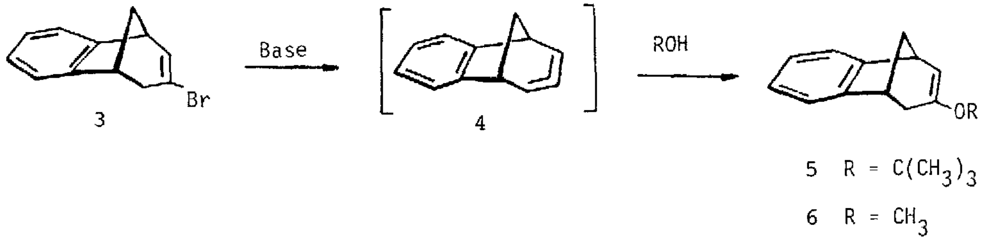
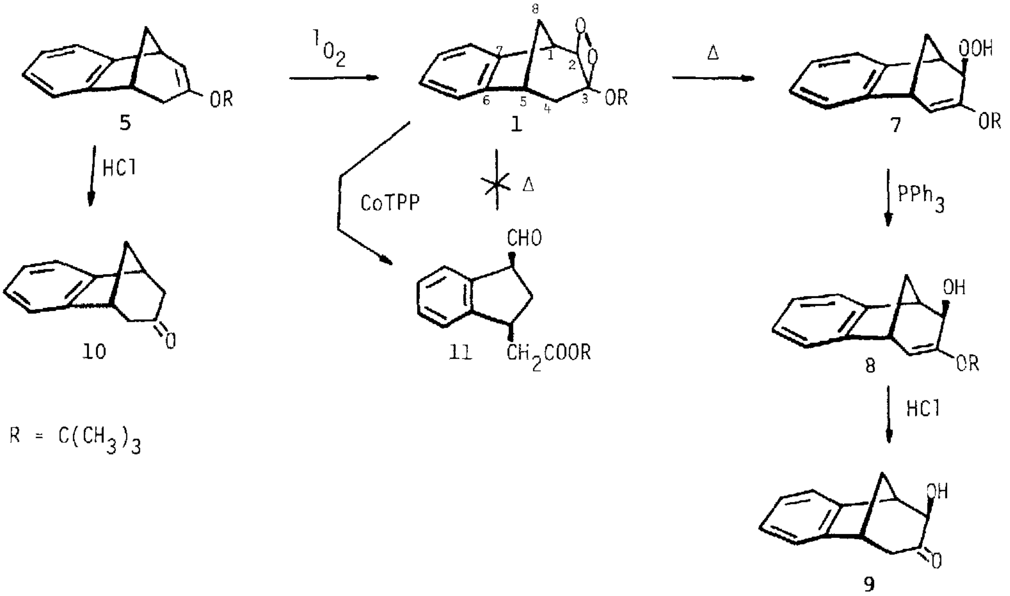
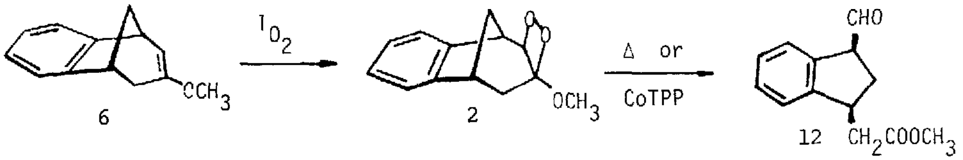


3-Bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene 3 was prepared by published method[4] and subjected to dehydrobromination with potassium tert-butoxide. Enol ether 5 was formed as the sole product. In an earlier publication[5] we reported that the dehydrobromination of 3 gives rise to the strained bicyclic allene 4 which was trapped by tert-butanol to form enol ether 5[5]. Attempted synthesis of 6 in the same way using $NaOCH_3$ as base did not reveal the formation of 6. However, 6 was obtained as a mixture with 5 by using potassium tert-butoxide and sodium methoxide in a ratio of 1:1. 5 and 6 were separated after column chromatography (Alumina, Grade III, eluting with petroleum ether) in yields of 10% and 17%, respectively. The products were identified by means of their spectral data and ready hydrolysis to the known ketone 10[4] with dilute HCl.



The enol ethers 5 and 6 in aprotic solvent (carbon tetrachloride) at -15 °C reacts rapidly and in high yields with singlet oxygen giving the corresponding dioxetanes 1 and 2. The dioxetanes 1 and 2 have been characterized by means of their ^1H-NMR data[6] and chemical reactions. The characteristic down field chemical shift (δ: 4.86 and 4.90 ppm in 1 and 2) of the proton directly attached to the dioxetane ring can be clearly seen. H_2 proton resonances in 1 and 2 appear as a doublet of doublets. The first splitting ($J = 3.6$ Hz) is arising from the bridgehead proton H_1. The second splitting originates from the internal proton H_8 ($J = 1.1$ Hz). The



fact, that a coupling between H_{8i} and H_2 is existing due to the M or W arrangement[7] indicates the proton H_2 which in turns proves the exo-configuration of the dioxetane rings.

On warm-up to room temperature, the dioxetane 1 decomposes. The ^{1}H-NMR spectrum of the decomposition product is consistent only with the structure 7 not with the expected product 11. The structure of the hydroperoxide 7 has been secured by double resonance experiments. Furthermore, reduction of hydroperoxide 7 with triphenylphosphine gave the corresponding alcohol 8 and subsequent hydrolysis with HCl afforded the exo-ketol 9 whose structure has been determined on the basis of ^{1}H- and ^{13}C-NMR data. The dioxetane 2 was quite stable at room temperature in solution. Upon heating to 50-60 °C it decomposed to the expected aldehyde-ester 12. The attempted isolation of 12 failed. On the other hand, both dioxetanes 1 and 2 were treated with Cobalt(II)-tetraphenylporphyrine[8] at low temperature. In both cases, the corresponding aldehyde-ester 11 and 12[9] were formed , although again isolation of these products failed.

Our results indicate clearly striking differences in the thermal behavior of the dioxetanes 1 and 2. The first one rearranges to the hydroperoxide 7 and the second one decomposes to aldehyde-ester. Thermal isomerization of endoperoxides to dioxetanes have been reported in the literature[10] but not the inverse case. More recently, dioxetane-hydroperoxide rearrangement has been observed by Krebs[11] in the case of cyclobutadiene-dioxetane. However, this rearrangement was catalyzed by HCl. To the best of our knowledge, we observe for the first time in the literature a dioxetane-hydroperoxide rearrangement under thermal conditions. The fact, that this rearrangement occurs under the exactly same reaction conditions only with 1 not with 2, indicates clearly that the steric factors arising from tert-butyl group play a dominating role for this unprecedented dioxetane-hydroperoxide conversion. Baumstark[12] and Lechtken[13] have observed that the stability of dioxetanes can be influenced by steric effects. An explanation was suggested in which steric interactions force the conformation of the substituent toward a twist boat which is resulting in lowering activation energy of the O-O bond cleavage. In the case of 1 steric repulsion is determining the mode of the decomposition reaction.

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6) 6: colorless liquid; ^{1}H-NMR (60 MHz, CCl_4, TMS); δ 1.63-2.66 (m, 4H), 3.15 (s, 3H), 3.15 (m, 2H), 4.8 (d, 1H), 6.73-7.15 (m, 4H); IR (CCl_4, cm^{-1}) 3065, 2960, 1640, 1470, 1370, 1210, 1170, 1120, 1040.

1: ^{1}H-NMR (60 MHz, TMS, CCl_4), 1.3 (s, 9H), 1.5-3.5 (m, 6H), 4.86 (dd, 1H), 6.95 (s, 4H).

2: ^{1}H-NMR (60 MHz, TMS, CCl_4), 2.0-3.5 (m, 6H), 3.43 (s, 3H), 4.90 (dd, 1H), 6.73-7.10 (m, 4H).

7: colorless liquid; ^{1}H-NMR (6o MHz, TMS, CCl_4) 1.25 (s, 9H), 2.14 (m, 2H), 3.30 (m, 1H), 3.67 (m, 1H), 4.1 (d, 1H), 5.6 (d, 1H), 6.86-7.40 (m, 4H), 91. (s, 1H); IR (neat, cm^{-1}); 3420, 3040, 3020, 2980, 1640, 1390, 1370, 1250, 1150, 1020.

9: colorless solid; mp 93-94 °C from CH_2Cl_2/n-hexane; ^{1}H-NMR (360 MHz, $CDCl_3$, TMS) 2.30 (dtt, A-part of AB-system, 1H), 2.37 (d, B-part of AB-system, 1H), 2.45 (br. d, A-part of AB-system, 1H), 2.93 (ddd, B-part of AB-system, 1H), 3.43 (m, 1H), 3.50 (m, 1H), 3.9 (dd, 1H), 7.16-7.35 (m, 4H); ^{13}C-NMR (90 MHz, TMS, $CDCl_3$) 211.14, 148.03, 142.23, 128.10, 127.64, 124.49, 123.41, 77.00, 46.52, 46.40, 39.30, 36.22; IR (KBr, cm^{-1}) 3620, 3090-3040, 2970, 1730, 1470, 1420, 1230, 1050. MS (70 eV) m/e 188.

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9) 11: ^{1}H-NMR (60 MHz, CCl_4, TMS) δ 1.4 (s, 9H), 1.8-2.63 (m, 4H), 3.25 (m, 1H), 3.65 (m, 1H), 7.1 (s, 4H), 9.53 (d, 1H).

12: ^{1}H-NMR (60 MHz, TMS, CCl_4) δ 1.7-2.9 (m, 4H), 3.2-3.8 (m, 2H), 3.56 (s, 3H), 7.1 (s, 4H), 9.50 (d, 1H).

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