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PERHYDROLYSIS OF γ-LACTONES
A NOVEL BAYER-VILLIGER OXIDATION.[1]

Waldemar Adam* and Ladislaus Szendrey

Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931, USA.

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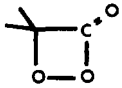
In our efforts to prepare novel cyclic peroxides, particularly α-peroxylactones 1,[2] β-peroxylactones 2,[3] and γ-peroxylactones 3,[4] the latter could possibly be prepared via perhydrolysis of the readily available γ-lactones 4. Since treatment of malonic acids with 98% H_2O_2 in $MeSO_3H$ afforded the corresponding malonoyl peroxides in high yield,[5] it was of interest to submit α,α, γ-trimethyl-γ-valerolactone (4a) and β,β,γ-trimethyl-γ-valerolactone (4b) to the above reaction conditions. In this communication we describe our unexpected results obtained in the perhydrolysis of the isomeric γ-lactones 4a and 4b.



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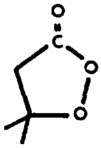

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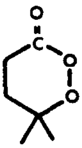

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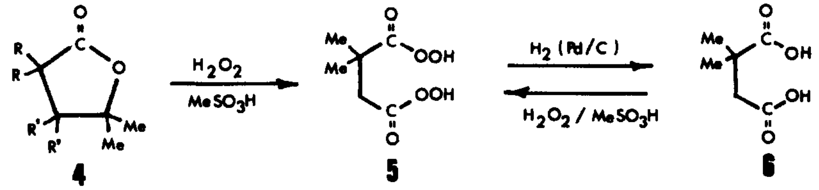
Treatment of α,α-dimethylsuccinic anhydride, prepared by acetic anhydride cyclization of α,α-dimethylsuccinic acid (6),[6] with methyl magnesium bromide afforded the pure, isomeric γ-lactones 4a (mp 43-44°) and 4b (mp 99-100° after numerous fractional crystallizations and distillations.[7] Subjection of the γ-lactones 4a and 4b to 98% H_2O_2(CAUTION!) in $MeSO_3H$ for 2 hrs at room temperature produced the same peroxidic material in over 90% yield. Catalytic reduction over Pd/C of the crude reaction product gave quantitatively α,α-dimethylsuccinic acid (6), characterized in form of its dimethyl ester by comparison of glpc retention times ir, nmr, and mass spectra with an authentic sample, prepared from 6 by esterification with diazomethane. Consequently, the initial peroxidic material had to be the diperoxy acid 5, as shown in eq 1. This assignment was confirmed by independent synthesis of the diperoxy acid 5, mp 54-55°, with explosive decomposition at 65° (98% pure by iodometric titration), from the succinic acid 6 and 98% H_2O_2 (CAUTION!) in $MeSO_3H$, and shown to be identical to the perhydrolysis product of the γ-lactones 4a and 4b.

(1)



a R = Me , R' = H
b R = H , R' = Me

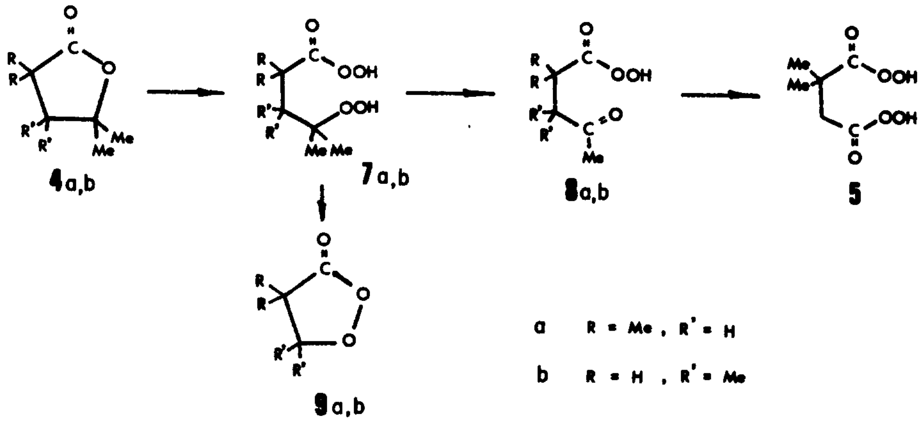
This unusual result is interpreted mechanistically in eq 2. Acid-catalyzed ring opening of the γ-lactones 4a and 4b and attack by hydrogen peroxide produces the intermediary γ-hydroperoxy peroxy acids 7a and 7b, respectively. Protonation of the hydroperoxide function and rearrangement of the γ-methyl leads to the γ-keto peroxy acids 8a and 8b, respectively, while fragmentation of the β,γ carbon-carbon bond of 4a,b and cyclization with the H_2O_2, gives the respective β-peroxylactones 9a and 9b, which were isolated in low yields (5-10%) by elution chromatography on silica gel of the crude perhydrolysis product, and characterized by ir, nmr, and mass spectra. The γ-keto peroxy acids 8a and 8b do not survive the H_2O_2-$MeSO_3H$ conditions and undergo Bayer-Villiger rearrangement of the γ-methyl group affording the same diperoxy acid 5. We verified the Bayer-Villiger rearrangement on levulinic acid, which was converted in high yield to diperoxy succinic acid with

98% H_2O_2 in $MeSO_3H$.[8]

In this unusual Bayer-Villiger rearrangement the γ-carboxy group must excercise a long range directing effect, since methyl migrates exclusively even in the γ-keto peroxy acid **8b** without migration of the disubstituted β-carbon.[9] In order to exclude the possibility that other than electronic factors are responsible for the observed migratory aptitudes, submission of 2-heptanone to the H_2O_2-$MeSO_3H$ treatment led to pentanol and acetic acid, after catalytic hydrogenation over Pd/C, the expected Bayer-Villiger products after hydrolysis of the ester.

We anticipate that for degradative and synthetic work the novel H_2O_2-$MeSO_3H$ reagent may prove useful. An additional advantage is the fact that after catalytic hydrogenation the alcohol and acid is obtained directly, rather than the ester as in the normal Bayer-Villiger oxidation.

(2)



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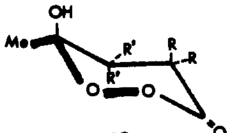
3. W.Adam and G. Santiago Aponte, *ibid.*, **94**, 4300 (1971).
4. W.Adam and L. Szendrey, *Chem. Commun.*, 1299 (1971).
5. W.Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).
6. J.K. Inglis, *Org. Syn. Coll. Vol.*, **1**, 249 (1932).
7. D.Currell, C.A. Grob, and S.W. Tam, *Helv. Chim. Acta*, **50**, 349 (1967).
8. The diperoxy succinic acid was somewhat difficult to isolate, and for this reason the crude reaction mixture was catalytically reduced over Pd/C, esterified with diazomethane, and the dimethyl succinate characterized by ir, nmr, and glpc retention times.
9. The preferential migratory aptitude of methyl over the β-carbon in **8**a,b may reflect a conformational effect dictated by the intermediate **10** (suggested by a referee), in which the methyl to γ-carbon bond can be anti-periplanar to the peroxide bond, as required for anionotropic 1,2-shifts, while the β,γ-carbon carbon bond cannot.



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