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NOVEL ACID HYDROLYSIS OF 2,3,5,6-DIEPOXY-2,5-DIMETHYL-1,4-BENZOQUINONE

Aspi B. Daruwala^a

^a Department of Chemistry, Purdue University, West Lafayette, Indiana

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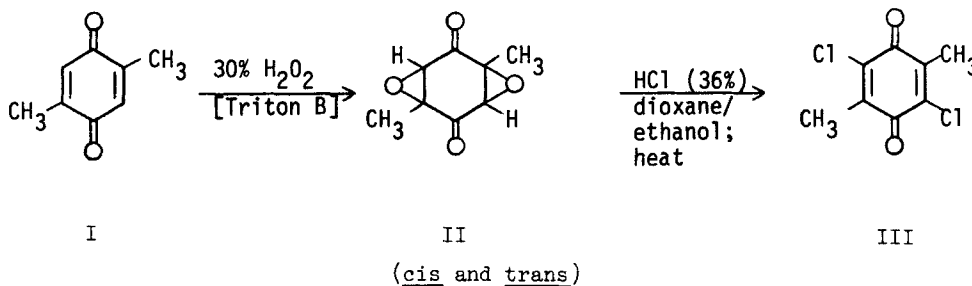
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NOVEL ACID HYDROLYSIS OF 2,3,5,6-DIEPOXY-2,5-DIMETHYL-1,4-BENZOQUINONE

Submitted by Aspi B. Daruwala
(3/10/77)

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

The hydrolysis of 2,3,5,6-diepoxy-2,5-dimethyl-1,4-benzoquinone (II)¹ investigated as a possible route to 3-hydroxy-6-chloro-2,5-dimethyl-1,4-benzoquinone (IV),² led instead to 3,6-dichloro-2,5-dimethyl-1,4-benzoquinone (III) in 69% yield.



EXPERIMENTAL

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 Spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60A spectrometer using TMS as the internal standard and all the chemical shifts are reported in δ values. Mass spectra were obtained on Hitachi RMV-6A Spectrometer at 70 eV.

cis- and trans-2,3,5,6-Diepoxy-2,5-dimethyl-1,4-benzoquinone (II).- To a stirred solution of I (6.8 g, 5 mmoles) in 200 ml of 3:1 dioxane/ethanol was added 20 ml of 30% hydrogen peroxide and 1.5 ml of Triton B. As the reaction proceeded, the yellow color disappeared and the solution became clear and colorless. Then it was stirred for 1 hr. and poured into 1 l. of ice water. The aqueous solution was extracted with methylene chloride (12 x 100 ml) and dried over anhydrous sodium sulfate. Removal of the solvent gave 5.2 g of II (61%) as a white crystalline product, mp. 86-88° IR (nujol): 1705 (C=O) 1140 cm^{-1} (epoxide); $^1\text{H NMR}$ (CDCl_3): δ 2.33 (s, 3H, Me), 3.56 (s, 1H, -OCH) for cis-isomer and 2.38 (s, 3H, Me) and 3.43 (s, 1H, -OCH) for trans-isomer; m/e 168 (M^+), 152, 125, 111, 99, 98, 83, 69, 55, 43 (base).

Anal. Calcd for $\text{C}_8\text{H}_8\text{O}_4$: C, 57.14; H, 4.80. Found C, 57.16; H, 4.91.

3,6-Dichloro-2,5-dimethyl-1,4-benzoquinone (III).- A solution of (925 mg, 5.5 mmoles) in 44 ml of 10:1 dioxane/ethanol and 20 ml of conc. HCl was heated to reflux for 2 hr. to accomplish complete solution and stirred at room temperature for 18 hrs. Dilution with 30 ml of water and cooling in an ice-bath yielded light yellow crystals which were filtered and dried to give 780 mg (69%), mp. 177-178°, lit.⁵ mp. 178°. IR (nujol): 1655 (quinone, C=O), 1605 cm^{-1} (C=C); $^1\text{H NMR}$ (CDCl_3): δ 2.35 (s, 6H, 2Me); m/e 206 ($\text{M}+2$), 204 (M^+), 178, 176, 169, 143, 115, 113, 68 (base).

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A RAPID AND MILD PROCESS FOR THE OXIDATION OF
2,3-DICHLORO-5,6-DICYANOQUINONE (DDQ) FROM
2,3-DICHLORO-5,6-DICYANOHYDROQUINONE (DDHQ)

Submitted by John W. Scott*, David R. Parrish and Fred T. Bizzarro

Chemical Research Department
Hoffmann-La Roche Inc.
Nutley, New Jersey 07110

The potent, and often quite selective oxidizing power of 2,3-dichloro-5,6-dicyanoquinone (DDQ, II) has led to its extensive use^{1,2} as a

