Pergamon

Tetrahedron Letters 40 (1999) 2069–2070

TETRAHEDRON LETTERS

Formation of *trans*-3-Hydroxy-4-phenylbutyrolactone from *trans*-Styrylacetic Acid and Aqueous $KHSO_5$

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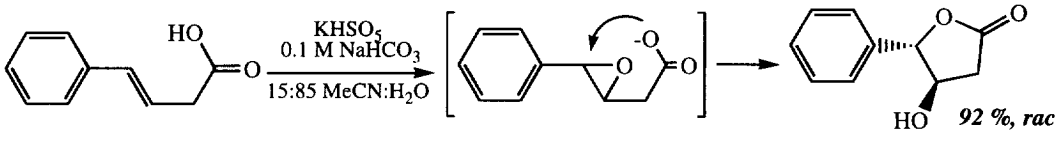
Received 21 December 1998; accepted 11 January 1999

Abstract: The formation of *trans*-3-hydroxy-4-phenylbutyrolactone from *trans*-styrylacetic acid mediated by aqueous $KHSO_5$ is described. The lactone is proposed to arise via an epoxide intermediate directly formed by the monopersulfate.

Keywords: Epoxidation, Lactonization, Monopersulfate

The use of aqueous media in organic transformations is attractive from both an economical and environmental perspective. In the arena of aqueous oxidative transformations, potassium monopersulfate ($KHSO_5$) has followed hydrogen peroxide as an oxidant of choice.[1] $KHSO_5$ has been used by many researchers by itself and in conjunction with ketones (to form dioxiranes) or with transition metal complexes in a number of epoxidations and other oxidative transformations.[1,2] In the course of studying Ni(II) and Co(II) mediated epoxidations in aqueous media, we screened a number of water-soluble alkenes for use as substrates. The results here highlight the nature of the olefin in epoxidation, and the effectiveness of monopersulfate itself as an epoxidizing agent.[3]

The oxidation of *trans*-styrylacetic acid was carried out in 15% acetonitrile in water (v/v) with $KHSO_5$. The reaction was maintained at basic pH (~8.5) by including 0.1 M $NaHCO_3$. For analysis, carboxylate components of the reaction were methylated with diazomethane,[4] and then analyzed by GC. Only a small amount of epoxide was detected, with the lactone, 3-hydroxy-4-phenylbutyrolactone,[5] as the major product. Under the basic conditions employed, this product presumably arises from intramolecular epoxide ring-opening by the



the carboxylate, resulting in the racemic lactone with a *trans* configuration between the phenyl and hydroxyl functional groups. After three hours reaction time at room temperature, the reaction yielded 92% lactone, 6% epoxide, and 2% unreacted starting material, as determined by GC. For comparison, the previous synthesis of this lactone utilized *meta*-chloroperbenzoic acid to form the epoxide followed by a basic aqueous work up (15%

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00167-7

yield).[6] Osmium catalyzed asymmetric dihydroxylation has been used in the formation of the *cis* lactone of this composition.[7]

The nature of the olefin is a significant feature of the above transformation. For comparison, the electron poor olefins *trans*-cinnamic acid and *p*-vinylbenzoic acid, under the same conditions, gave only their individual epoxides in 5% and 30% yield, respectively. It is noteworthy that neither a ketone nor metal based catalyst was required to generate the epoxide via dioxirane or metal-oxo species. These features highlight $KHSO_5$ as an effective epoxidizing agent itself under certain conditions and with selected substrates. Given the number of species found in the decomposition of $KHSO_5$,[8] we propose that various cosolvents (acetonitrile, ethanol, etc.) not only enhance substrate solubility, but may suppress or absorb the nonproductive decomposition products, such as sulfate radical,[9] available to monopersulfate.

Acknowledgments: JDV thanks the National Institutes of Health for a Training Fellowship (GM-08537). This work was supported by a grant from the National Institute of General Medical Sciences (GM-49860).

References and Notes

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5. Systematic name: dihydro-4-hydroxy-5-phenyl-2(3H)-furanone. *Trans*-Styrylacetic acid (0.059 g, 0.36 mmol) was dissolved in 5 mL 15% acetonitrile in water with the addition of 1 eq. KOH (0.36 mL 1 N solution) in a 50 mL round-bottom flask. $NaHCO_3$ (1 mL, 1M) was added, followed by $KHSO_5$ (272 mg dissolved in 3.6 mL water, 1.5 mmol 'O' atom as determined by iodometric titration) and the reaction mixture stirred for 3 h. The products of the reaction were extracted by layering the aqueous solution with diethyl ether (20 mL) and acidifying with 1 N HCl (10 mL) followed by two further extractions with diethyl ether (15 mL). Diazomethane was introduced into the combined ethereal extracts to methylate the acidic products, which were then analyzed by various methods. The lactone was purified by column chromatography (silica gel, 100% $CHCl_3$ to elute methylated starting material and epoxide, 10% MeOH in $CHCl_3$ to elute product). Analytical GC: RT = 15.44 min. on a 15 m DB-5 column at 110-170° C ramp at 5° C/min. GC-EIMS (EI -70 eV) *m/z* (relative intensity) 178 [M^+] (9), 150 [M^+- CO] (12), 107 [M^+- $C_3H_3O_2$] (100), 79 (53), 77 [$C_6H_5^+$] (33). IR (KBr plate, oil) ν (cm^{-1}): -OH, 3433; C-H, 2952, 2919, 2850; C=O, 1781; C-O, 1198,1167; C-O, 1057, 1043. ^1H NMR ($CDCl_3$, δ): 7.2-7.5 (m, 5H, aromatic CH), 5.40 (d, 1H, γ-CH, J_{HH} = 3.4), 4.49 (ddd, 1H, β-CH, J_{HH} = 3.4, 3.9, 6.4), 3.85 (br s, 1H, OH), 2.87 (dd, 1H, α-CH_a, J_{HH} = 17.8, 6.4), 2.60 (dd, 1H, α-CH_b, J_{HH} = 17.8, 3.9). ^{13}C NMR ($CDCl_3$, δ): 175.3 (C=O), 136.6 (*ipso*-Ph), 128.8 (*m*-Ph), 128.6 (*p*-Ph), 125.0 (*o*-Ph), 87.9 (γ-CH), 74.4 (β-CH), 36.9 (α-CH_2).
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