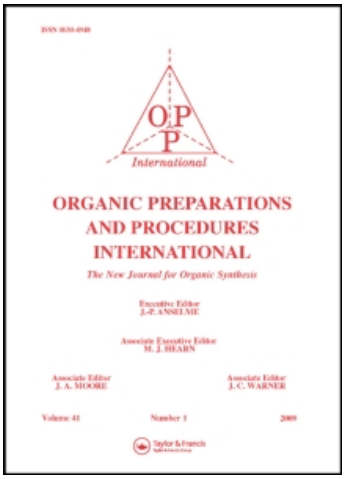

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A FACILE SYNTHESIS OF 3,4-DIHYDRO-1,5-BENZODIOXEPIN-2-ONES

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A FACILE SYNTHESIS OF 3,4-DIHYDRO-1,5-BENZODIOXEPIN-2-ONES

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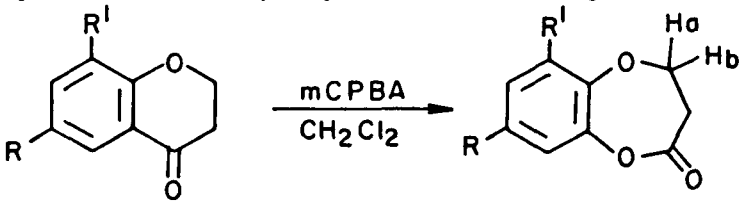
The oxidation of chromones and 3-formylchromones with m-chloroperbenzoic acid was previously reported[1,2] to afford 3-hydroxychromones. We now report the facile one-step synthesis of 3,4-dihydro-1,5-benzodioxepin-2-ones (IIa-e) in 60% yield by the Baeyer-Villiger



I II

a) R= R'=H; b) R=CH3, R'=H ; c) R=H, R'=CH3 ; d) R=Cl, R'=H ; e) R=Br, R'=H

oxidation of chromanones (Ia-e) using m-chloroperbenzoic acid. Eiden and Schmiz[3] reported the synthesis of IIa by the ring expansion of chromanone (Ia) by first oxidation with hydrogen peroxide/perchloric acid to give 2-hydroxyphenoxypropionic acid followed by cyclization with acetic anhydride furnished IIa.

The structures of IIa-e were established by physical methods and by an authentic synthesis of IIa in 20% yield by condensation of catechol and b-chloropropionyl chloride.

TABLE 1. Spectral and Analytical Data of 3,4-Dihydro-1,5-benzodioxepin-2-ones (IIa-e)

Compd	mp. (°C)	Yield[c] (%)	UV λ_{max}^{MeOH} (log ε)	^{1}H NMR ($CDCl_3$/TMS_{int}) δ ppm	M^+andother fragments	Elemental analysis Calcd(Found) C	H
IIa	oil	60	208 (4.128) 215 (4.118) 275 (3.470)	2.81(t,J=6Hz,2H, C_3-H),4.26(t,J=6Hz, 1H,C_{4a}-H),4.4(t,1H, C_{4b}-H,7.15(m,4H, aromatic)	164,121 110, 56, 55	65.85 (65.82)	4.87 (4.84)
IIb	58	62	205 (4.069) 218 (3.794) 280 (3.329)	2.33 (s,3H,C_8-CH_3), 2.84(t,J=6Hz,2H, C_3-H),4.32(t,J=6Hz) 1H,C_4-H_a),4.51(t, J=6Hz,1H,C_4-H_b), 6.98 (m, 3H, aromatic)	178,135 124,56,55	67.41 (67.38)	5.61 (5.59)
IIc	46	60	208 (4.120) 218 (4.198) 278 (3.412)	2.32 (s,3H,C_6-CH_3), 2.81(t,J=6Hz, 2H, C_3-H),4.20(t,J=6Hz, 1H,C_4-H_a),4.32(t,J=6Hz 1H,C_4-H_b),7.20(m, 3H,aromatic)	178,135 124,56,55	67.41 (67.38)	5.61 (5.59)
IId	87	61	207 (4.171) 230 (3.694) 282 (3.375)	2.81 (t,J=6Hz, 2H, C_3-H),4.21(t,J=6Hz, 1H,C_4-H_a),4.40(t, J=6Hz,1H,C_4-H_b), 7.10(m,3H,aromatic)	198,155 144,56,55	54.54 (54.52)	3.53 (3.51)
IIe	74	59	207 (4.318) 220 (3.940) 285 (3.463)	2.88 (t, J=6Hz, 2H, C_3-H),4.24(t,J=6Hz, 1H,C_4-H_a),4.55(t, J=6Hz,1H,C_4-H_b), 7.16(m,3H,aromatic).	242,199 188,56,55	44.62 (44.60)	2.89 (2.85)

a) Carbonyl absorption at ~ 1765 cm^{-1}. b) Lit. [3] bp. 153° c) Yield calculated from 4-chromanone.

The exclusive formation of 3,4-dihydro-1,5-benzodioxepin-2-ones (IIa-e) rather than the alternative products 1,4-benzodioxepin-5-ones may be ascribed to the greater migratory aptitude of an aryl over a methylene group in the Baeyer Villiger oxidation step.

EXPERIMENTAL SECTION

The starting compounds Ia (bp. 78-80°), Ib (mp. 35-36°), Ic (mp. 29.5°), Id (mp. 105°) were prepared by literature procedure.[4] Ie (mp. 77°, lit.[5] mp. 77°) was also prepared for the first time by the same procedure.[4]

General Procedure for the Oxidation of 4-Chomanones with m-CPBA.- 4-Chromanones (1a-e) (0.01 mol) and m-chroroperbenzoic acid (1.72 g, 0.01 mol) were heated under reflux in dry dichloromethane (50 ml) over a period of 15-18 hrs. The m-chlorobenzoic acid which had precipitated during reflux was removed by filtration and the filtrate was concentrated. The resulting residue dissolved in ethyl acetate and the solution was washed with 2% aqueous sodium bicarbonate (3 x 30 ml) and dried over anhydrous sodium sulphate and evaporated. The colorless semi-solids were crystallized from pet. ether (IIb, c) or benzene (IId, e) to yield colorless needles. IIa was purified by preparative thin layer chromatography to yield a colorless oil.

Synthesis of 3,4-Dihydro-1,5-benzodioxepin-2-one (IIa) from Catechol.- Catechol (1.1 g, 0.01 mol) and β–chloropropionyl chloride (1.2 g, 0.01 mol) was stirred at room temperature in 5% methanolic potassium hydroxide solution (50 ml) for 6 hrs. The solvent was removed under reduced pressure. The residue (1.0 g) was chromatgraghed over silica gel (ACME, 200 mesh, 60 g). Elution with benzene (200 ml) gave a crude liquid which was purified by preparative TLC, to yield 3,4-dihydro-1,5-benzodioxepin-2-one (IIa) as colourless liquid (0.41 g, 20%), identical in all respects (Co-tlc and Superimposable IR) with IIa prepared as described above.

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A SIMPLE PREPARATION OF 1-HYDROXYPYRENE

Submitted by (04/04/88)

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1-Hydroxypyrene, a metabolite[1] of pyrene, is a valuable intermediate for the synthesis of