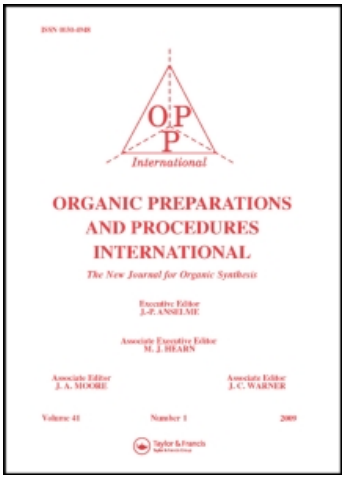

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ONE-STEP PREPARATIONS OF ISOMERIC (2,6-DIOXACYCLOHEXYL)PHENOLS

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6. Purity 96-98% by nmr. Identified by nmr (90 MHz), ir, elemental analysis and ms. Product I is not entirely stable to typical gc injector temperatures and partially decomposes to give pyridine, 2-cyanopyridine and other unidentified products. The nmr shifts given differ only slightly from those in the literature.[1] The ir spectrum displayed a weak nitrile band. The compound did not decompose appreciably after two months of refrigerated storage at 4°.

ONE-STEP PREPARATIONS OF ISOMERIC (2,6-DIOXACYCLOHEXYL)PHENOLS†

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The utility of (2,6-dioxacyclohexyl)phenols as immediate precursors of insecticides[1] as well as synthetic intermediates of 1,2,3-trisubstituted aromatic compounds is well documents.[2] It has been long known that hydroxybenzaldehydes do not undergo acetalization under acid-catalyzed conditions in satisfactory yields.[3,4] Reasonable yields of acetal[4] are obtained when the phenolic group is blocked as an acetate. Acetalization followed by alkaline hydrolysis generates the phenolic acetal[2] in overall yields of 60%. This report describes a one-step procedure to transform

hydroxybenzaldehydes into dioxane acetals without prior protection of the phenolic group.

This acetalization method is based on the procedure of Kantlehner and co-workers,[5] which utilizes the dimethylformamide-dimethyl sulfate adduct[6] as a promoter, the alcohol in three-fold excess and an organic solvent. Yields and physical data are given in the Table. The procedure gives excellent yields for phenolic dioxane acetals, but is less successful for the preparation[7] of phenolic dioxolane acetals. The ease of the procedure as well as its success in the presence of phenolic groups make it attractive for future applications.

EXPERIMENTAL SECTION

Typical Procedure.- To a solution of 15 g (0.12 mol) of 3-hydroxybenzaldehyde in 75 ml of dichloromethane, were added in one portion, 28.1 g (0.37 mol) of 1,3-propanediol and 31.8 g (0.16 mol) of DMF-DMS adduct. After being stirred at room temperature for 24 hrs, the reaction mixture was cooled to 0° and slowly quenched with 22 ml (0.16 mol) of triethylamine while the temperature was maintained at or below 5°. This reaction mixture was extracted with five 100-ml portions of ethyl ether. The combined ethereal extracts were successively washed with three 50-ml portions of NaOAc-saturated 5% aqueous $NaHSO_3$[9] and two 50-ml portions of NaOAc-saturated brine. After drying over Na_2SO_4, the solvent was removed under vacuum, leaving 19.3 g (87%) of a cream-colored solid, which was pure by ^1H NMR. Recrystallization from benzene afforded an analytically pure sample.

TABLE. Yields and Physical Data for Isomeric (2,6-Dioxacyclohexyl)phenols

Benzaldehyde	% Yield	mp (°C, solvent)	(lit. mp.)
2-Hydroxy	79	58-59.5 (hexane-PhH)	(55-58)[a]
3-Hydroxy	87	109.5-110.5 (PhH)	(109-110)[a]
4-Hydroxy	87[c]	122.5-124 (PhH)	(126-129)[b]

a) Ref. 4 b) Ref. 10 c) Ref. 11

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7. The yields for the isomeric (2,5-dioxacyclopentyl)phenols were as follows: 2-hydroxy (16%); 3-hydroxy (57.4%); and 4-hydroxy (0%).

8. All spectral analyses confirmed structural assignments.

9. The use of NaOAc saturated bisulfite or sodium chloride solution was necessary to avoid hydrolysis of the product, which occurs extensively when it is not done.

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11. This particular isomer has to be extracted with ca. 10% DCM in Et_2O because of its low soluility in pure ether. Extraction with pure DCM is not advisable since it also extracts some byproducts.