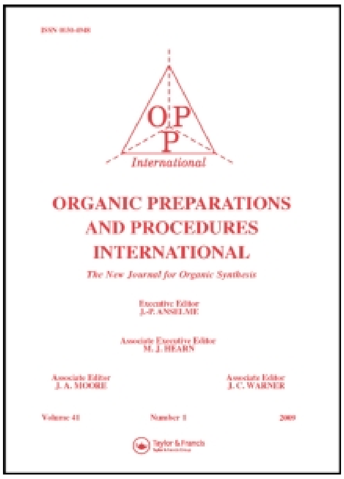

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IMPROVED PREPARATION OF SURFACTANTS DERIVED FROM SUCROSE WITH ULTRASOUND

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IMPROVED PREPARATION OF SURFACTANTS DERIVED FROM SUCROSE WITH ULTRASOUND

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(10/09/97)

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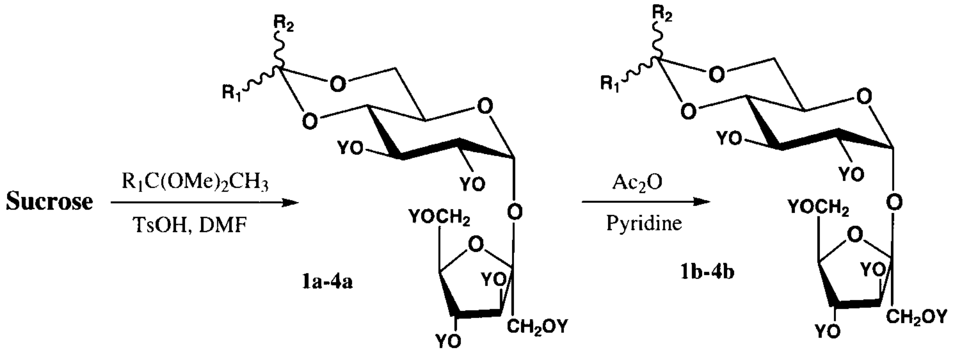
Sugars can constitute the hydrophilic part of a detergent, as they possess a number of hydroxy groups. For this purpose, they must be associated with a lipophilic tail, generally a linear alkyl chain. Such saccharide-derived materials have become a focus of great interest[1] because (*i*) they have excellent detergent properties, (*ii*) sugars are vast natural and renewable resources and (iii) they may confer biodegradability properties to their derivatives. Thus it seemed useful to improve procedures affording amphiphilic saccharide derivatives. Within this framework, we recently described the synthesis of long-chain acetals derived from sucrose and trehalose, which are a new class of nonionic surfactants, stable in basic medium.[2] We have shown that the direct transacetalation of sugar with 2,2-dimethoxyalkanes constitutes an efficient procedure to obtain such acetals. This paper deals with transacetalation of sucrose improved with ultrasonic irradiation, which is well known to increase the rate and the yield of a number of organic reactions.[3]

In accordance with the published procedure,[2] the transacetalation of sucrose carried out in *N,N*-dimethylformamide with 2,2-dimethoxyalkanes and in the presence of *p*-toluenesulfonic acid afforded as major product the monoacetal **1a**, **2a**, **3a** or **4a** in approximately 30% yield. The acetals were identified on the basis of NMR spectral data ; their peracetylated derivatives (**1b**-**4b**) were also prepared. The optimum reaction time was found to be 120 minutes.



In the present study, the transacetalation was carried out under the same conditions with the use of ultrasonic irradiation. The progress of the reaction, monitored by TLC, revealed that the optimal reaction time had decreased to 10 minutes.The rate of solubilization of the starting sucrose was considerably increased with respect to standard conditions.[2] Compounds **1-4b** were obtained in approximately 45% yields (Table). Various catalysts were examined (camphorsulfonic acid, pyridinium *p*-toluenesulfonate, sulfuric acid) and the optimum yields were obtained with *p*-toluenesulonic acid. The use of other solvents such as acetonitrile, dichloromethane, acetone or the reagent itself led to no reaction or yields smaller than 5%.

Thus, it is clear that the application of ultrasound both accelerates the rate and substantially improves the yield of the transacetalation.

EXPERIMENTAL SECTION

All solvents were routinely distilled and dried prior to use. Evaporations were performed under reduced pressure. Ultrasonic reactions were performed with a 20 KHz generator connected to a direct immersion horn dipping in a round bottom cylindrical reactor controlled (water bath) in order to maintain the temperature below 35°. Column chromatography was carried out with Silica Gel 60 (E.

Merck 70-230 mesh), and TLC was carried out on precoated plates (E. Merck 5724), with detection by charring with H_2SO_4. Optical rotations were mesured at 20°, on a Jasco DIP-370 polarimeter (*c* 1.0, chloroform or water).

TABLE. Yields and $[\alpha]_D^{20}$ of Products

Cmpd	$R_1 = (CH_2)_nCH_3$ n	R_2	Y	Yield[a] (%)	Yield[b] (%)	$[\alpha]_D^{20}$
1a	4	CH_3	H			+17
1b	4	CH_3	Ac	30±2	45+2	+53
2a	7	CH_3	H			+25
2b	7	CH_3	Ac	30±2	45+2	+43
3a	10	CH_3	H			+25
3b	10	CH_3	Ac	30±2	45+2	+46
4a	5	$(CH_2)_5CH_3$	H			+37
4b	5	$(CH_2)_5CH_3$	Ac	30±2	45+2	+55

a) With stirring. b) With sonication.

Acetalation. General Sonochemical Procedure.- In the sonochemical reactor, 3.42 g of sucrose (0.01 mol), 50 mL of anhydrous *N,N*-dimethylformamide, 2 mol equiv of 2,2-dimethoxyalkane and a catalytic amount of *p*-toluenesulfonic acid were introduced ; the mixture was then subjected to ultrasound for 10 minutes. It was then neutralized with sodium carbonate, filtered, and the solvent was evaporated under reduced pressure. The syrupy residue was acetylated (1:1 acetic anhydride-pyridine, 0°) and the acetal obtained was purified by column chromatography (eluent 1:1 ethyl acetate-cyclohexane). Physical constants and spectral NMR data were identical to those previously described.[2]

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AN EFFICIENT AND FACILE PROCEDURE FOR DEPROTECTION OF 1,1-DIACETATES USING ANHYDROUS FERROUS SULFATE

Submitted by (10/27/98)

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The selective protection and deprotection of functional groups is of great importance in synthetic organic chemistry. 1,1-Diacetates have received increasing attention because these compounds are stable to oxidants,[1,2] readily prepared,[3-9] easily converted to the parent aldehydes and can serve as alternatives to acetals for selective protection of aldehydes.[10] They are also important starting materials for the synthesis of valuable intermediates of Diels-Alder reaction.[11,12] A literature search revealed that a number of methods have been reported for the conversion of 1,1-diacetates to corresponding aldehydes.[13] The following reagents have been used: alcoholic sulfuric[1] or hydrochloric[2] acid, either sodium hydroxide or potassium carbonate in aqueous THF,[3] boron triiodide-N,N-diethylaniline complex,[14] ceric ammonium nitrate (CAN) coated on silica gel in dichloromethane,[15] neutral alumina,[16] potassium phenoxides,[17] montmorillonite K-10 and KSF[18-20] and expensive graphite.[21] While each of the above methods has its own merit, some have drawbacks such as the need to use strong acids which other functional groups may not tolerate and long reaction time (no detailed results are given),[3] low yield (<66%),[14] and the use of microwave heating.[16,18,19]

Anhydrous ferrous sulfate has been used as a catalyst for organic reactions.[22-24] We previously developed an efficient procedure for preparation of 1,1-diacetates from aldehydes using a catalytic quantity of anhydrous ferrous sulfate.[22] Herein we report a rapid and efficient procedure for the deprotection of 1,1-diacetates catalyzed by anhydrous ferrous sulfate in refluxing dichloromethane, benzene or toluene.

$$\underset{\mathbf{1}}{RCH(OAc)_2} \xrightarrow[\Delta,\ \text{solvent}]{FeSO_4} \underset{\mathbf{2}\ (96\text{-}99\%)}{RCHO + Ac_2O}$$

When solutions of 1,1-diacetates (**1**) in dichloromethane, benzene or toluene are heated at reflux in the presence of anhydrous ferrous sulfate, the corresponding aldehydes (**2**) are obtained in