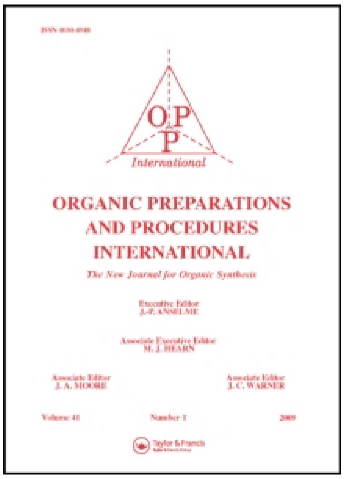

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN EFFICIENT AND CONVENIENT PROCEDURE FOR ESTER HYDROLYSIS

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To cite this Article Khurana, J. M. and Sehgal, Arti(1994) 'AN EFFICIENT AND CONVENIENT PROCEDURE FOR ESTER HYDROLYSIS', Organic Preparations and Procedures International, 26: 5, 580 — 583
To link to this Article: DOI: 10.1080/00304949409458062
URL: http://dx.doi.org/10.1080/00304949409458062

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AN EFFICIENT AND CONVENIENT PROCEDURE FOR ESTER HYDROLYSIS

Submitted by
(01/28/94)

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Ester hydrolysis, an important transformation is usually catalyzed by acids or bases.[1] Although substrates sensitive to hydrolytic conditions may be cleaved by a number of reagents under neutral conditions,[2] most of these reagents have limited applications and are either costly or not readily available. Both acidic and alkaline hydrolyses are equilibrium reactions; however for preparative purposes ester hydrolyses are almost always performed in basic solution in order to shift the equilibrium. To overcome the problem of a heterogeneous system, micellar catalysis[3] and phase transfer catalysis[4] have recently been employed, though the improvement under these conditions is not significant. Moon *et al.*[5] have reported the use of ultrasound to catalyze two-phase ester saponifications. Therefore, search for a simple method for ester hydrolysis having wider application is still warranted. We now report that the hydrolysis of a variety of esters of aromatic, aliphatic and fatty acids with sodium hydroxide in aqueous dimethylformamide proceeds in nearly qnantitative yields in 15-60 min

TABLE. Hydrolysis of Esters

Ester	DMF (mL/g)	NaOH[a] (%)	Time (min)	Method	Yield (%)	mp (lit.)[7] (°C)
Methyl benzoate	5	15	15	A	89	120-122(120-122)
Ethyl benzoate	5	15	45	A	88	121-122(120-122)
n-Propyl benzoate	10	60	45	B	69[b]	120(120-122)
iso-Propyl benzoate	15	60	45	B	73[b]	120-121(120-122)
n-Butyl benzoate	15	60	45	C	36[c]	120(120-122)
Phenyl benzoate	5	30	45	C	87	120-121(120-122)
Methyl phenylacetate	5	15	30	A	90	78-80(78-79)
Ethyl phenylacetate	5	15	60	A	91	78-79(78-79)
iso-Propyl phenylacetate	10	30	45	B	85	79(78-79)
n-Propyl phenylacetate	5	30	30	B	83	77-78(78-79)
n-Butyl phenylacetate	5	30	30	B	85	79(78-79)
Methyl cinnamate	5	15	45	A	88	130-132(133-134)
Ethyl cinnamate	10	30	45	A	85	130-133(133-134)
Methyl p-nitrobenzoate	5	15	15	A	88	236-238(239-241)
Methyl 3,5-dinitrobenzoate	5	15	30	A	90	207(207)
Ethyl 3,5-dinitrobenzoate	5	15	30	A	90	207(207)
Methyl *p*-anisate	5	15	30	B	91	183(184)
Methyl *o*-chlorobenzoate	5	15	30	B	95	137-138(138-140)
Methyl *m*-chlorobenzoate	5	15	30	B	96	154-156(153-157)
Methyl *p*-chlorobenzoate	5	15	30	A	93	238-242(239-241)
Dimethyl phthalate	5	15	30	B	79	210-211(210)
Dioctyl phthalate	10	60	45	C	85	208-210(210)
Methyl aleurate	5	15	60	B	94	99-100(100-101)
Methyl stearate	20	45	45	B	96	68(67-69)
Methyl laurate	20	45	45	B	86	42-(44-46)
Methyl palmitate	20	45	45	B	90	63(61-64)
Methyl *cis*-α-phenylcinnamate	10	45	45	B	98	172-173(172-174)
Dimethyl succinate	5	15	15	D[d]	93	152-153(154)[e]
Diethyl oxalate	5	15	15	D[d]	92	194-196(196)[e]
Diethyl malonate	5	15	15	D[d]	95	144-145(146)[e]
Ethyl acetate	5	15	60	D[d]	72	134-135(134)[e]
Cyclohexyl formate	5	15	30	D[d]	82	155-156(152)[e]

a) A volume of 10 mL sodium hydroxide solution was used per gram of ester. b) The aqueous portion was not extracted because of partial solubility of *n*-propyl alcohol and isopropyl alcohol. c) The yield is low because of benzoic acid solubility in *n*- butanol. d) Yield based on S-benzyl thiouronium salt recovered. e) mp/lit. mp of S-benzylthiouronium salts are given.[7]

by stirring the mixture at ambient temperature. The method is superior to micellar catalysis, phase-transfer catalysis or the use of ultrasound with two-phase reactions. While cyano, alkoxy, thioether, amino and formyl groups are unaffected, amides and anilides are cleaved partially (20-35%) under these reaction conditions.[6]

EXPERIMENTAL SECTION

Dimethylformamide (SRL) and sodium hydroxide (Qualigens) were used as received. The esters were obtained from commercial sources or were prepared by known procedures. All the melting points were recorded on Tropical Labequip apparatus and are uncorrected. The IR spectra were recorded on Perkin-Elmer model 621 and Shimadzu model 435.

Typical Procedure.- The ester (1 g) was stirred with 10 mL of aqueous sodium hydroxide (see Table) and dimethylformamide (see Table 1) at ambient temperature. After disappearance of the ester (tlc), the reaction mixture was worked up according to methods A, B, C or D.

Method A: The reaction mixture was acidifed with 6N HCl. The solid carboxylic acid was collected and the aqueous portion was extracted with ether (3x10 mL). The combined ethereal extract was dried ($MgSO_4$) and concentrated on a rotary evaporator to yield more of the acid.

Method B: The reaction mixture was acidified with 6N HCl and the carboxylic acid so obtained was collected and dried in air.

Method C: The reaction mixture was extracted with ether (3x10 mL) to remove alcohol and the aqueous portion was then acidified with 6N HCl and the carboxylic acid thus obtained was collected and dried in air.

Method D: The carboxylic acids which are water soluble or are liquids can be obtained by acidification of the reaction mixture with 6N HCl but were isolated as their S-benzylthiouronium salts for characterization purposes. The reaction mixture was treated with 1N HCl dropwise till the solution is just alkaline (pH 7-7.5). A saturated aqueous solution of S-benzylthiouronium chloride was added to the above solution and the S-benzylthiouronium carboxylate deposited within 5 minutes.[7] The product was collected and dried in air. All compounds were identified by their mps and their mixture mp without recrystallization. The carboxylic acids can be regenerated by treatment of S-benzylthiouronium carboxylate with 6N HCl or ion exchange resins.

Acknowledgement.- One of us AS is grateful to UGC, New Delhi, India for financial support as JRF.

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CONVERSION OF AROMATIC NITRILES TO ALDEHYDES BY SODIUM *tris*(DIALKYLAMINO)ALUMINUM HYDRIDES

Submitted by (12/13/93)

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A new class of reducing agents, dialkylamino substituted derivatives of lithium aluminum hydride appears to be useful for the selective conversion of organic functionalities.[1] The chemoselective reduction of aromatic nitriles to the corresponding aldehydes in the presence of aliphatic nitriles using lithium *tris*(dihexylamino)aluminum hydride (LTDHA)[1g,2] seems to be especially promising, since this conversion is important in organic synthesis.[2-4] Very recently, we synthesized various alkoxy and dialkylamino substituted derivatives of sodium aluminum hydride and applied them in the selective reductions of organic groups. In the course of this study, we found that like LTDHA,[1g,2] the dialkylamino substituted derivatives of sodium aluminum hydride achieve the selective conversion of aromatic nitriles to aldehydes in good yields at room temperature. This communication describes such