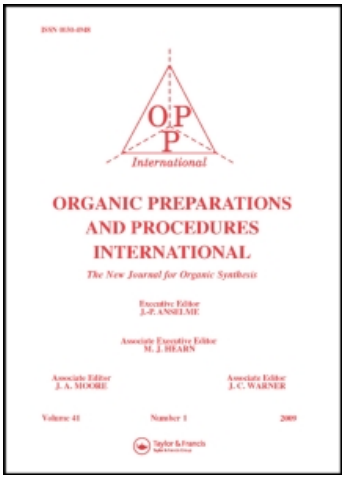

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A NEW, FACILE METHOD FOR DETRIFLUOROACETYLATION OF ESTERS WITH TRIETHYLAMINE PRETREATED SILICA GEL

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A NEW, FACILE METHOD FOR DETRIFLUOROACETYLATION OF ESTERS WITH TRIETHYLAMINE PRETREATED SILICA GEL

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(01/13/99)

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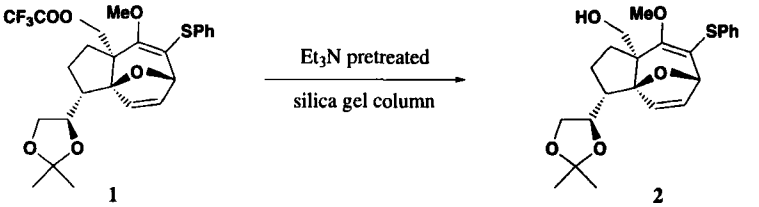
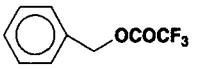
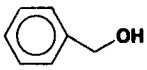
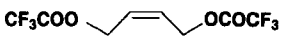
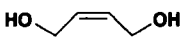
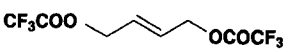
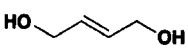
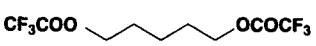
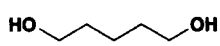
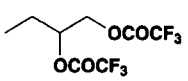
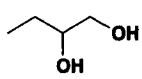
Trifluoroacetyl is a useful protective group for alcohols especially those hindered hydroxyl groups,[1] and excellent selectivity may be achieved for one of two similar hydroxyl groups even with the highly reactive trifluoroacetylation reagents.[2] However, only few studies on detrifluoroacetylation have been reported.[3] In the course of our studies on the total synthesis of pseudolaric acid A, we found a very mild, facile and straightforward method for detrifluoroacetylation by just simply using a Et_3N pretreated silica gel column.



In order to assertain the generality of this method, a number of trifluoroacetates and *bis*-trifluoroacetates were tested. The results of these experiments are shown in **Table 1**. All the products displayed with physical constants and spectra data consistent with literature data.

Table 1. Detrifluoroacetylation of Ester

Trifluotoacetate	Alcohol	Yield (%)
$CH_3(CH_2)_{16}CH_2OCOCF_3$	$CH_3(CH_2)_{16}CH_2OH$	97
		100
		95
		95
$CH_3(CH_2)_8CH_2OCOCF_3$	$CH_3(CH_2)_8CH_2OH$	97
		96
		96

The detrifluoroacetylation is carried out under very mild conditions, which are particularly suitable for complex molecules containing several protecting groups such as compound **1**. The yields are nearly quantitative. This method offers easy work-up, and the deprotection of the starting materials and the purification of the products could be conducted on the same column. Meantime, we checked the results in parallel with control experiment using the silica gel column without pretreatment with triethylamine. No deprotection of compound **1** occurred.

EXPERIMENTAL SECTION

TLC analysis was performed on silica gel plates (0.25mm thickness) with F_{254} indicator. Flash chromatography was performed on 200-400 mesh silica gel from Aldrich. mps were determined on a Buchi 510 apparatus and are uncorrected. Infrared spectra were obtained as KBr pellets in Nicole Magna 750. ^{1}H NMR spectra were recorded on a Bruker AMX-400MHz spectrometer with tms as internal standard in $CDCl_3$ solution. ^{13}C NMR spectra were recorded on the same instrument. $[a]_D$ was measured on Perkin-Elmer 241MC. Mass spectra and high resolution mass spectra were measured on a Varian MAT-711 and MAT-95, respectively.

Deprotection of Compound 1. Typical Procedure.- To a column of silica gel (5g) was added Et_3N (10 drops), and the column was washed with ether until the pH of the eluent is 7.5-8. Trifluoroacetic ester **1**[4] (50 mg, 0.1mmol) was subsequently added and the column was then eluted with petroleum ether-ether (1:1) under low pressure. Removal of the solvent of the eluent gave 40 mg (95%) of alcohol **2** as a white solid, mp. 98-100°. ^{1}H NMR (400MHz, C_6D_6): δ 7.40 (2H, d, *J* = 7.6Hz), 7.10 (2H, t, *J* = 7.6Hz), 7.00 (1H, t, *J* = 7.6Hz), 6.28 (1H, dd, *J* = 5.9, 1.7Hz), 5.80 (1H, d, *J* = 5.9Hz), 4.78 (1H, d, *J* = 1.7Hz), 4.50-4.60 (1H, q, *J* = 8.0Hz), 4.00 (1H, t, *J* = 8.0Hz), 3.70-3.80 (4H, m), 3.44-3.60 (2H, dd, *J* = 12Hz), 2.65 (1H, m), 2.10-2.20 (2H, m), 1.68-1.80 (2H, m), 1.26 (3H, s), 1.20 (3H, s). ^{13}C NMR (100MHz, C_6D_6): δ 164.6, 137.3, 132.9, 128.7, 128.5, 128.3, 126.2, 110.1, 108.9, 96.3, 80.9, 75.4, 68.4(2C), 65.0, 60.4, 47.1, 31.4, 27.8, 26.2, 24.0. MS (m/z): 416(M^+, 100), 384(5), 327(53), 311(18), 215(23), 182(20), 123(10), 59(41). IR (film): 3525, 1602, 1581, 1479, 1371, 1210, 1066, 1049, 973, 840, 740 cm^{-1}. HRMS: Calcd for $C_{23}H_{28}O_5S$: 416.1641. Found: 416.1658. $[\alpha]_D^{20}$ = -10.1° (c 0.015, acetone).

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4. Selected data of compound **1** (oil): HRMS: Calcd for $C_{25}H_{27}F_3O_6S$: 512.1463; Found: 512.1472. ^{1}H NMR (300MHz, C_6D_6): δ 7.40 (2H, d, *J* = 8.0Hz), 7.00 (2H, t, *J* = 8.0Hz), 6.90 (1H, t , *J* =

8.0Hz), 6.28 (1H, d J = 5.9Hz), 5.90 (1H, d, J = 5.9Hz), 4.70 (1H, s), 4.40-4.50 (1H, m), 4.10 (2H, dd, J = 12Hz), 3.90 (1H, m), 3.70 (3H, s), 2.55 (1H, m), 2.10 (1H, m), 1.60 (4H, m), 1.40 (3H,s), 1.10 (2H, m). IR (film): 2980, 1786, 1412, 1261, 798 cm $^{-1}$. MS(m/z): 512 (M^+, 40), 497(10), 403(25), 327(35), 342(10), 101(100). $[\alpha]_D^{20}$ = -25.3° (c 0.13, acetone).

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BENZYLTRIPHENYLPHOSPHONIUM DICHROMATE AS A MILD REAGENT FOR THE OXIDATION OF ORGANIC COMPOUNDS

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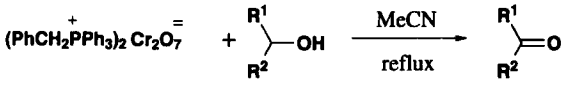
This paper describes the oxidation of organic compounds under non-aqueous and aprotic conditions using benzyltriphenylphosphonium dichromate (**1**, $PhCH_2PPh_3)_2$ Cr_2O_7) which is very easily prepared by mixing an aqueous solution of benzyltriphenylphosphonium chloride with CrO_3 in 3 N HCl at room temperature. This reagent, a stable orange powder which may be stored for month without loss of activity, is soluble in acetonitrile, chloroform and dichloromethane and slightly soluble in carbon tetrachloride, ether and hexane. The oxidation of organic compounds with **1** proceeds well in acetonitrile reflux. Benzylic and allylic alcohols **2** are oxidized to the corresponding carbonyl compounds in high yields; benzoin was converted to benzil in excellent yield (Table 1). In contrast, the oxidation of allylic alcohols with manganese dioxide require a large excess of this reagent and long reaction times.[1] Because of the low reactivity of aliphatic alcohols, only benzylic and allylic alcohols could be converted into the corresponding carbonyl compounds.



(1)

1 **2** **3**

We also found that the oxidation of **1** with oximes (**4**) and substituted hydrazones (**5**) previously accomplished by a number of reagents,[2,3,5] in refluxing acetonitrile gave the corresponding carbonyl compounds (*Scheme 1*). No further oxidation to the carboxylic acids was observed (Tables 2 and 3). The mechanism of the product reaction is not readily apparent at this time.

A noteworthy advantage of this reagent lies in its ability to selectively oxidize oximes in the presence of other oxidizable functions such as alcohols and double bonds. When we retreated an equimolar amount of oxime (**4h** or **4l**) was treated with **1** in the presence of benzyl alcohol, the oxime was