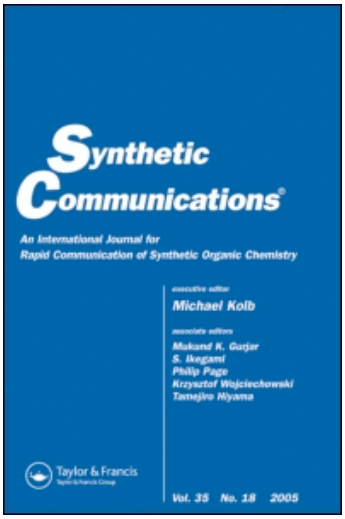

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Preparation of Monoalkyl Terephthalates: An Overview

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Preparation of Monoalkyl Terephthalates: An Overview

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Abstract: Terephthalic acid can be readily converted to the corresponding monoalkyl terephthalate in high yield, via a two-step procedure. This method is advantageously compared to the more representative methods described in the literature. The purification of the expected monoester, a crucial problem for this synthetic pathway, is discussed, and an original procedure has been developed.

Keywords: dialkyl terephthalates, monoalkyl terephthalates, monohydrolysis, terephthalic acid

INTRODUCTION

Preparation of monoesters of symmetric dicarboxylic acids on a gram scale remains a challenge for synthetic chemists when the corresponding cyclic anhydrides are not readily available. Even recently, articles dealing with

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this problem have been published, starting either from the diacid or the dimethyl or diethyl esters.

When the diacid is the starting material, various supports acting as adsorbents[1] such as alumina or catalysts[2] (ion-exchange resins) are used in the presence of alkylating agents, and high selectivity is claimed by each author or research group. On the other hand, diesters require either selective enzymatic[3] or basic monohydrolysis under anhydrous[4] or aqueous[5] conditions. Although enzymatic hydrolysis is only used in specific cases, basic hydrolysis seems to be more general, and authors often discussed the versatility of their own method (e.g., Niwayama's procedure,[6] which has been applied successfully to several classes of aliphatic diesters).

Interesting, alternative ways are reported in the literature:

- esterification of a formyl-containing acid followed by oxidation of the formyl group to obtain the monoester of the symmetric diacid[7] and
- carboxylation of arylcopper or arylpalladium compounds.[8]

In the latter case, the availability of the starting material is the crucial point, and it can be more difficult to obtain than the monoester itself.

We were particularly interested in the preparation of monoesters of terephthalic acid **2** and describe here an easy-to-handle ester monohydrolysis of various dialkyl terephthalates **1** using solutions of potassium hydroxide in the corresponding alcohols. A comparison to the most representative methods described in the literature is also provided.

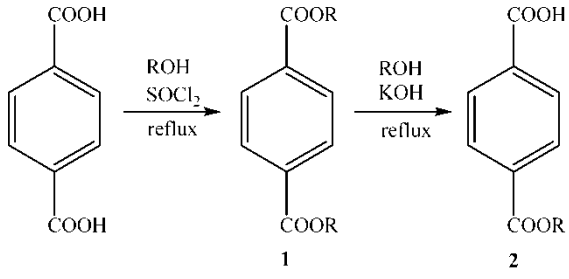
RESULTS AND DISCUSSION

We decided first to investigate the use of alumina as an adsorbent to transform specifically one of the acid groups to the corresponding ester. We therefore tried to adsorb terephthalic acid on commercial alumina following the procedure described in the literature.[1] Unfortunately, only traces of terephthalic were retained on alumina, unlike what was reported by Chihara et al.[1]

We also investigated the feasibility of a monohydrolysis of various diesters of terephthalic acid **1** in a basic medium (Scheme 1).

The latter have been prepared following a procedure often used in the laboratory (large excess of thionyl chloride added to an alcoholic solution of the diacid). The yields are reported in Table 1 and are generally more than 90% for primary alcohols, they obviously decrease for secondary alcohols (39% for isopropanol) because of the steric hindrance. No reaction has been observed when tertiobutanol was used.

Several procedures for monohydrolysis have been described in the literature,[5] generally dedicated to the formation of the monomethyl ester as starting material for different purposes.



R = Me, Et, Pr, *i*-Pr, Bu

Scheme 1.

Surprisingly, the ratios of potassium hydroxide/diester of terephthalic acid reported in the literature[5] are not exactly equal to one. Indeed, a slight excess of potassium hydroxide is used by some authors even though Hotten[5a] reported high yields of crude monomethyl terephthalic acid using a ratio of potassium hydroxide/dimethyl terephthalate equal to 0.97.

We therefore decided to evaluate the value of this ratio, and we observed that the best results were obtained when the value is logically equal to 1.

The solvent used is generally the corresponding alcohol, in order to avoid transesterification, but authors generally have not specified if anhydrous conditions are required. Nevertheless, we clearly observed an increase of terephthalic acid formation closely related to the presence of water.

The purification of the monoester obtained following this procedure is another crucial step, but still poorly described in the literature.

All the previous reports indicated that the expected monoester is always contaminated by small amounts of terephthalic acid as a by-product. The

Table 1. Preparation of dialkyl terephthalates

				Mp (°C)	
Entry	R	Product	Yield (%)	Found	Literature[a]
1	Me	1a	99	140–141	141–142
2	Et	1b	89	46–47	44
3	Pr	1c	99	29–31	31
4	*i*-Pr	1d	39	57–59	55–56
5	Bu	1e	95	Oil[b]	6

[a]See Ref. [9].
[b]At room temperature.

authors claimed that this monoester can be purified by recrystallization from water or acetone. Conversely, we observed that although purity really increases, traces of terephthalic acid are still observable by thin-layer chromatography (TLC).

However, terephthalic acid can be efficiently eliminated from the crude product when the latter is dissolved in a potassium hydroxide solution and quickly filtered to eliminate what remains in suspension.

Although the yields of monoesters decrease because of the presence of appreciable amounts of the latter in the filtration residues, this was the only practical way to obtain pure (diacid free especially) monoesters of terephthalic acid. This easy-to-handle procedure has been succesfully applied for all the monoesters listed in Table 2.

The low yield observed for monobutyl ester of terephthalic acid is only attributable to the poor solubility of potassium hydroxide in n-butanol.

In summary, we have clearly demonstrated that the easiest and less expensive way to prepare monoalkylesters of terephthalic acid consists of the monohydrolysis of the corresponding diester in the alcohol used for the preparation of the diester. The latter can be easily obtained in high yields from thionyl chloride in the corresponding alcohol.

High purity can be reached following the original procedure we describe here.

EXPERIMENTAL

Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were expressed in parts per million and were recorded on Bruker-AC 250-MHz spectrometer. The chemicals shifts were obtained with $CDCl_3$ and DMSO-d_6 as solvent and TMS as internal standard. Melting points were determined on a Stuart SMP3 binocular and are uncorrected. Mass spectra for diester were measured with Hewlett Packard 5971A electron impact (70 eV) mass spectrometer, equipped with a Hewlett Packard 5890 series II gas chromatograph.

Table 2. Monohydrolysis of dialkyl terephthalates

				Mp (°C)	
Entry	R	Product	Yield (%)	Found	Literature[a]
1	Me	2a	77	219–220	230
2	Et	2b	72	168–169	171
3	Pr	2c	72	130	127–129
4	*i*-Pr	2d	62	164	166
5	Bu	2e	13	123–125	122–124

[a]See Ref. [9].

General Procedure for the Preparation of Dialkyl Terephthalates

A solution of terephthalic acid (1.0 g, 6 mmol) and corresponding alcohol (50 mL) was refluxed for 30 min. Thionyl chloride (18 mL, 20 eq) was added dropwise, and the mixture was maintained 4 to 10 h under reflux. After being cooled to room temperature, the solvent was removed under reduced pressure. The mixture was extracted twice with ethyl ether (50 mL) and washed with a basic (potassium hydroxide) solution. The combined organic layers were dried over $MgSO_4$. Removal of the solvent allowed as to obtain the diester as a pure product. Yields: 99% for **1a**, 89% for **1b**, 99% for **1c**, 39% for **1d**, 95% for **1e**.

Data

Terephthalic acid dimethyl ester (**1a**)**:** ^{1}H NMR ($CDCl_3$): 3.95 (s, 6H, -O-CH_3), 8.10 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 52.4 (-O-CH_3), 129.5 (CH_{Ar}), 133.9 (C_{Ar}), 166.2 (C═O); GC-MS/EI: m/z (%): 194 (M^+, 25), 179 (4), 163 (100), 135 (24), 120 (9), 103 (15), 92 (4), 76 (17).

Terephthalic acid diethyl ester (**1b**)**:** ^{1}H NMR ($CDCl_3$): 1.41 (t, $J = 7.1$ Hz, 6H, -O-CH_2-$\underline{C}H_3$), 4.41 (q, $J = 7.1$ Hz, 4H, -O-$\underline{C}H_2$-CH_3), 8.10 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 14.1 (-O-CH_2-$\underline{C}H_3$), 61.2 (-O-$\underline{C}H_2$-CH_3), 129.2 (CH_{Ar}), 133.9 (C_{Ar}), 165.6 (C═O); GC-MS/EI: m/z (%): 222 (M^+, 13), 194 (21), 177 (100), 149 (62), 121 (13), 104 (18), 76 (20).

Terephthalic acid dipropyl ester (**1c**)**:** ^{1}H NMR ($CDCl_3$): 1.04 (t, $J = 7.3$ Hz, 6H, -O-CH_2-CH_2-$\underline{C}H_3$), 1.81 (m, 4H, -O-CH_2-$\underline{C}H_2$-CH_3), 4.31 (t, $J = 6.7$ Hz, 4H, -O-$\underline{C}H_2$-CH_2-CH_3), 8.10 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 10.4 (-O-CH_2-CH_2-$\underline{C}H_3$), 22.0 (-O-CH_2-$\underline{C}H_2$-CH_3), 66.9 (-O-$\underline{C}H_2$-CH_2-CH_3), 129.4 (CH_{Ar}), 134.1 (C_{Ar}), 165.8 (C═O); GC-MS/EI: m/z (%): 250 (M^+, 4), 191 (100), 167 (94), 149 (85), 104 (34), 41 (24).

Terephthalic acid diisopropyl ester (**1d**)**:** ^{1}H NMR ($CDCl_3$): 1.39 [d, $J = 6.7$ Hz, 12H, -O-CH-($\underline{C}H_3$)$_2$], 5.27 [sep, $J = 6.7$ Hz, 2H, -O-$\underline{C}H$-(CH_3)$_2$], 8.08 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 21.9 (-O-CH-($\underline{C}H_3$)$_2$), 69.0 [-O-$\underline{C}H$-(CH_3)$_2$], 129.4 (CH_{Ar}), 134.5 (C_{Ar}), 165.4 (C═O); GC-MS/EI: m/z (%): 250 (M^+, 6), 209 (23), 197 (56), 167 (34), 149 (100), 121 (17), 104 (24), 76 (28), 59 (45), 43 (42).

Terephthalic acid dibutyl ester (**1e**)**:** ^{1}H NMR ($CDCl_3$): 0.99 (t, $J = 7.3$ Hz, 6H, -O-CH_2-CH_2-CH_2-$\underline{C}H_3$), 1.48 (m, 4H, -O-CH_2-CH_2-$\underline{C}H_2$-CH_3), 1.77 (m, 4H, -O-CH_2-$\underline{C}H_2$-CH_2-CH_3), 4.35 (t, $J = 6.4$ Hz, 4H, -O-$\underline{C}H_2$-CH_2-CH_2-CH_3), 8.10 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 13.6 (-O-CH_2-CH_2-CH_2-$\underline{C}H_3$), 19.1 (-O-CH_2-CH_2-$\underline{C}H_2$-CH_3), 30.6 (-O-CH_2-$\underline{C}H_2$-CH_2-CH_3), 65.1

(-O-$\underline{C}H_2$-CH_2-CH_2-CH_3), 129.3 (CH_{Ar}), 134.0 (C_{Ar}), 165.7 (C═O); GC-MS/EI (m/z): 278 (M^+, 2), 235 (2), 223 (77), 205 (100), 177 (2), 167 (79), 149 (72), 132 (2), 121 (24), 104 (19).

General Procedure for the Synthesis of Monoesters of Terephthalic Acid

To the starting diester (10 mmol), 30 mL of corresponding alcohol was added, and the mixture was heated for 15 min. Potassium hydroxide (1 eq) was poured into the solution, and then the mixture was heated for 3.5 h under reflux. The mixture was cooled, and the alcohol was evaporated. The resulting crude product was dissolved in water and extracted with dichloromethane. The aqueous layer was acidified with concentrated hydrochloric acid. The precipitate was then filtered or extracted with ethyl ether, dried over magnesium sulphate, and concentrated under reduced pressure.

Data

Monomethyl ester (**2a**)**:** ^{1}H NMR ($CDCl_3$): 3.76 (s, 3H, -O-CH_3), 7.91 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 51.2 (-O-CH_3), 128.2 (CH_{Ar}), 128.4 (CH_{Ar}), 132.4 (C_{Ar}), 132.9 (C_{Ar}), 165.0 (C═O), 166.1 (C═O).

Monoethyl ester (**2b**)**:** ^{1}H NMR ($CDCl_3$): 1.43 (t, $J = 7.3$ Hz, 3H, -O-CH_2-$\underline{C}H_3$), 4.42 (q, $J = 7.3$ Hz, 2H, -O-$\underline{C}H_2$-CH_3), 8.17 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 13.6 (-O-CH_2-$\underline{C}H_3$), 60.6 (-O-$\underline{C}H_2$-CH_3), 128.6 (CH_{Ar}), 128.9 (CH_{Ar}), 133.2 (C_{Ar}), 134.2 (C_{Ar}), 165.1 (C═O), 166.9 (C═O).

Monopropyl ester (**2c**)**:** ^{1}H NMR ($CDCl_3$): 0.67 (t, $J = 7.3$ Hz, 3H, -O-CH_2-CH_2-$\underline{C}H_3$), 1.44 (m, 2H, -O-CH_2-$\underline{C}H_2$-CH_3), 3.92 (t, $J = 6.8$ Hz, 2H, -O-$\underline{C}H_2$-CH_2-CH_3), 7.71 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 10.0 (-O-CH_2-CH_2-$\underline{C}H_3$), 20.7 (-O-CH_2-$\underline{C}H_2$-CH_3), 65.4 (-O-$\underline{C}H_2$-CH_2-CH_3), 127.6 (CH_{Ar}), 128.3 (CH_{Ar}), 132.5 (C_{Ar}), 133.6 (C_{Ar}), 164.3 (C═O), 165.9 (C═O).

Monoisopropyl ester (**2d**)**:** ^{1}H NMR ($CDCl_3$): 1.00 [d, $J = 6.1$ Hz, 6H, -O-CH-($\underline{C}H_3$)$_2$], 4.85 [sep, $J = 6.1$ Hz, 1H, -O-C$\underline{H}$-(CH_3)$_2$], 7.69 (m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 21.7 [-O-CH-($\underline{C}H_3$)$_2$], 68.6 [-O-$\underline{C}$H-(CH_3)$_2$], 129.2 (CH_{Ar}), 129.4 (CH_{Ar}), 134.0 (C_{Ar}), 134.7 (C_{Ar}), 165.2 (C═O), 167.1 (C═O).

Monobutyl ester (**2e**)**:** ^{1}H NMR ($CDCl_3$): 0.59 (t, $J = 7.3$ Hz, 3H, -O-CH_2-CH_2-CH_2-$\underline{C}H_3$), 1.08 (m, 2H, -O-CH_2-CH_2-$\underline{C}H_2$-CH_3), 1.38 (m, 2H, -O-CH_2-$\underline{C}H_2$-CH_2-CH_3), 3.93 (t, $J = 6.7$ Hz, 2H, -O-$\underline{C}H_2$-CH_2-CH_2-CH_3), 7.68

(m, 4H, H_{Ar}); ^{13}C NMR ($CDCl_3$): 12.8 (-O-CH_2-CH_2-CH_2-CH_3), 18.2 (-O-CH_2-CH_2-CH_2-CH_3), 29.7 (-O-CH_2-CH_2-CH_2-CH_3), 64.2 (-O-CH_2-CH_2-CH_2-CH_3), 128.4 (CH_{Ar}), 128.6 (CH_{Ar}), 132.9 (C_{Ar}), 134.0 (C_{Ar}), 164.8 (C═O), 166.5 (C═O).

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