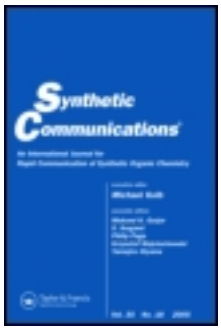

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Efficient Routes to Racemic and Enantiomerically Pure (S)-Binol Diesters

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EFFICIENT ROUTES TO RACEMIC AND ENANTIOMERICALLY PURE (S)-BINOL DIESTERS

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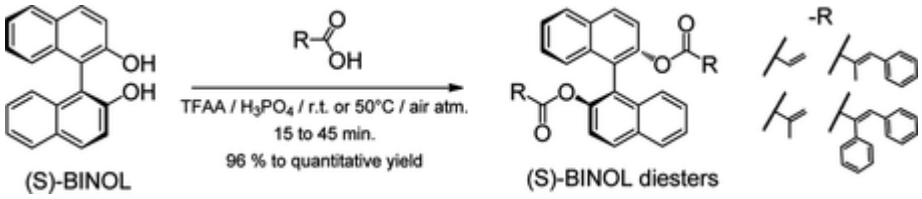
Abstract

A systematic study for esterification procedures to the synthesis of BINOL diesters is described. Reaction conditions with TFAA and 85% H_3PO_4 were selected as the best procedure to prepare enantiomerically pure (S)-BINOL diesters **VIII** to **XI** with almost quantitative yields and very low reaction times.

[Supplementary materials are available for this article. Go to the publisher's online edition of *Synthetic Communications*® for the following free supplemental resource(s): Full experimental and spectral details.]



KEYWORDS: diols, esterification, phase-transfer catalysis, diesters, BINOL, C_2 symmetry.

INTRODUCTION

Since 1990, the enantiomeric atropoisomers of 1,1´-binaphthyl-2,2´-diol (BINOL, **I**) have become one of the most widely used ligands for both stoichiometric and catalytic asymmetric reactions.[1] The preparation of racemic BINOL and its resolution has been widely studied, and some well-established methods are reported.[2]Stereoselectivity control is based in the utilization of molecules from the C_n or D_n groups of symmetry that allow the prediction of enantioselectivity due to the existence of only one reactive species. Under this supposition, chiral atropoisomers become very interesting, especially those corresponding to binaphtyl systems. The potential of **I** as a ligand for metal-mediated catalysis was first recognized in 1979 by Noyori in the reduction of aromatic ketones and aldehydes.[1g] BINOL itself, however, does not always give satisfactory results in asymmetric catalysis, and since Noyori's discovery there has been an ongoing interest in modified BINOL ligands. The rigid structure, thermal stability and the C_2 symmetry of the chiral binaphthyl molecules play an important rol in assymetric induction. In the last few years, BINOL derivatives have become attractive moleculeswith applications in chiral supramolecular recognition, crystal engineering, electro optical materials and polymers, among others.[3-6]These type of binaphtyl compounds are often synthetized using enantiomerically pure BINOLas the starting material easily transforming the 2,2´-hydroxy groups into other functional groups.[7]

RESULTS AND DISCUSSIONS

Several diastereoselective synthesis of macrocycles have been developed using chiral auxiliary groups and rigid organic templates.[8a–d]As part of our research work on the

behavior of diesters derived from diols with C_2 symmetry and as precursors of new macrodiolides,[8e]we now report a systematic study of some efficient and optimized synthetic routes to saturated and unsaturated (±)-BINOL diestersthrough five different procedures, with the aim of determining the best reaction conditions,easy to handle, with high efficiency and minimum environmental impact, comparing the direct acylation using carboxylic acids with those mediated by acid derivatives (Scheme 1). Once the best selected procedure was chosen, it was applied for the synthesis ofenantiomerically pure (S)-BINOL diesters**VIII** – **XI** starting from (S)-BINOL.[9]Among some uses, these compounds have great application in odontology, [10] and are a source of chiral dendrimers for use in asymmetriccatalysis.[11]

Direct acylation of alcohols with carboxylic acids is preferred over acylation with anhydrides (poor atom economy) or acid chlorides (moisture sensitive). The main disadvantage of direct acylation is the unfavorable chemical equilibrium that can be overcome by a large excess of one of the reagents, or removing water by Dean-Stark distillation. Besides, phenols or naphthols are usually too unreactive to give useful yields by this procedure. **Unlike –OH group of alcohols (pka values between 16–18), -OH group of phenols is more acidic(pka values between 8–10) being less reactive towards esterification and therefore** requires activation of the corresponding carboxylic acid used. This can be achieved either *via* conversion of carboxylic acid to more reactive functional groupsor *in situ* activation in the presence of coupling reagents.[12] It is important to remark, however, that some of these methods present some disadvantages

related to the use of volatile and environmentally harmful organic solvents and reagents, low or moderate yields and long reaction times.

With the aim of finding esterification procedures with high efficiency and minimum environmental impact, we report here the results obtained in the synthesis of diesters**II** to **VII**comparing the direct acylation of BINOL (**I**) using carboxylic acids with the reaction mediated by acid derivatives (Scheme 1) . This initial studies were conducted using racemic **I**, but the procedures were equally valid for the enantiomerically pure BINOL diesters**VIII – XI** synthetized later.

First, racemic (±)-BINOL (**I**) was prepared according to well known procedures.[2a] (*S*)-BINOL was purchased from Aldrich, although there are established methods to resolve (±)-BINOL.[2d]The esterification of **I** was achieved following five different reaction conditions (Methods A-E) and the results obtained are summarized in Table 1.[13]The progress of the reactions was monitored by TLC of silica gel and, after completion, quantified by GC-MS through a standard curve generated from isolated pure product.

The first method is one of the most versatile procedures of direct esterification that uses dicyclohexylcarbodiimide (DCC) and dimethyl-aminopyridine (DMAP).[14]The reaction probed to be insensitive to steric hindrance in the carboxylic acid and proceeded at room temperature with reaction times between 1–4 h.In this case, the reaction was carried out in a toluene/p-toluensulfonic acid media instead of the classical (and non recommendable)benzene commonly used in this esterification method (Method **A**, Table

1, entries 1, 6, 11, 16, 21 and 26). The yields observed in the crude reaction products are high (between 81 - 98 % , determined by **GC**-MS analysis) but it has the disadvantage that N-acylurea generated as a byproduct must be carefully separated by filtration through celite and silica gel 60 column chromatography. This causes some lost in the final yield about 10%.

One particular transesterification methodology, which also uses carboxylic acids and phenols mixtures as substrates, is trifluoracetic acid anhydride (TFAA) /H_3PO_4-mediated direct O-acylation, that has obtained a new impulse recently.[15] Here, we extended the method to the synthesis of BINOL diesters through this single-step and metal-free process (Method **B**, Table 1, entries 2, 7, 12, 17, 22 and 27). The reactions were performed at room temperature or with gentle warming (50ºC) depending on the carboxylic acid used, under **air** atmosphere. To our pleasure, all the reactions tested were ready between 15 to 45 minutes with almost quantitative yields of the racemic BINOL diesters**II** – **VII** and no formation of the monoester was observed. A simple extraction and washing with diluted NaOH solution provides the target diesters almost pure. In the case of compounds **VI** and **VII**,yields are relatively minor probably due to some steric hindrance in the carboxylic acid that also delayed the esterification reaction.[16]

On the other hand, it is well known that there are some advantages in the use of acyl chlorides or acid anhydrides instead of the Fisher esterification. Some of them are increased speed, performance, milder conditions and lack of reversibility. The main disadvantagesare that not always the desired acid chloride is available and its preparation

involves some special care due to its moisture sensitivity. Taking into account that alkoxide ion treatment with acid halides and other derivatives is a common way to access esters in some cases, NaHcan be used as a base and is very easy to handle (air manipulation). Thus, the course of the racemic BINOL (**I)** esterification reaction was analyzed using the corresponding acyl chloride, NaH and THF at room temperature (Method **C**, Table 1, entries 3, 8, 13, 18, 23 and 28). Unfortunately, diesters**IV**, **V**, **VI** and **VII** (entries 13, 18, 23 and 28, Table 1) could not be obtained and only unreacted (±)-BINOL and the corresponding monoester was observed. This suggests the possibility that, in these cases, the lack of reactivity is due to a strong intramolecular coordination of the sodium cation with the alcoxide anion and the carboxylic group when the first esterification reaction is completed and could hinder diesterification. According to previous studies referred to etherification reactions, [17- 18] crown ethers can prevent this undesired association by solvation of the sodium cation and increasing the nucleophilicity of the anion.So, we decided to study the same reaction conditions (NaH / THF / r.t.) but now adding 18-crown-6 (Scheme 2).

As can be seen from Table 1, (Method **D**, entries 4, 9, 14, 19, 24 and 29, Table 1) better performance was found compared with Method C in almost every case (75–95% except entry 24).Besides, this procedure is very suitable for its simplicity: the mixture was stirred at room temperature and when the reaction finished,the crude product was quenched with KBr saturated solution. Column chromatography purification on silica gel 60 provided the desired diesters**II – VII**in good yields.

Finally, the esterification procedure of (±) BINOL (**I)**was studied with acyl chlorides in a phase transfer catalytic (PTC) media (Method **E**, Table 1, entries 5, 10, 15, 20, 25 and 30). The biphasic system wasdichloromethaneand aqueous NaOH in the presence of a quaternary ammonium salt such as $Bu_4N^+Cl^-$ (Scheme 3).[19]NaOH is critical for good performance, but its concentration cannot exceed 30% since it can result in the hydrolysis of the resulting ester.[20]The optimum conditions for this esterification include the use of 0.03 equivalents of catalyst, dichloromethane as solvent and low temperature (0°C to r.t.). The observed yields for this procedure ranged between good to very good (53–95%) in moderate reaction times (12–24 h). The diesters**II** – **VII**were isolated by simple **phase** separation, washed with aqueous sodium bicarbonate, dried and purified on silica gel 60 column chromatography.

Once the optimum conditions for the synthesis of BINOL diesterswere fixed (Method **B,** TFAA/H_3PO_4, r.t. or 50° C, air atm.), this procedure was applied to obtain the desired enantiomerically pure (S)-BINOL diesters V**III** – **XI**. As expected, the products were obtained with excellent to quantitative yields and all the reaction times were between 15 to 45 min (Scheme 4).

In summary, we present here a comparative study of different procedures modifications leading to optimize synthetic routes to saturated and unsaturated BINOL diesters, racemic or enantiomerically pure, with excellent yields. Some of these methods demonstrated to be excellent and very efficient as in the case of Method **B**, which proved to be smooth and free from special care on the preparation and/or preconditioning of an acyl chloride.

In the case of Methods D and E (NaH / crown ether and NaOH / PTC respectively), both are very appropriate not only because of the good yields observed but also for the simplicity and mild reaction conditions. We have synthesized six racemic diesters and four enantiomerically pure diesters (**VIII**–**XI**) which are, to our knowledge, absolutely new. All the new compounds are characterized by a thorough analysis of their ^{1}H, ^{13}C-NMR, **GC**-MS and IR spectra. This promising preliminar results encouraged us for future studies with substituted BINOLs.

EXPERIMENTAL

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Tetrahydrofuran (THF) and toluene ($PhCH_3$) were distilled from sodium benzophenoneketyl under nitrogen. NaH was purchased from Fluka as 80% dispersion in mineral oil and must be rinsed with dry THF before use under inert atmosphere. Dry CH_2Cl_2 was achieved by simple storage of the solvent over activated 3 A˚ molecular sieves. Thin layer chromatography was performed on Merck precoated silica gel 60 F254 plates and visualization was accomplished with UV light and/or 5% ethanol solution of phosphomolibdic acid. Silica gel (Merck, 230–400 mesh) was used for column chromatography. Melting points were recorded on a Büchi Melting Point B-545 instrument and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 300 MHz spectrometer (300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C) at 23º C. Chemical shifts (δ) are given in ppm downfield relative to TMS (^{1}H and ^{13}C) and coupling constants (J) are in Hz. Mass spectra were obtained with a GC/MS instrument (HP5-MS capillary column, 30 m / 0.25 mm / 0.25 mm) equipped with 5972 mass selective detector operating at 70 eV

(EI).High resolution mass spectra (HRMS) were recorded on a Finnigan Mat 900 (HR-EI-MS).Compounds described in the literature were characterized by comparison of their ^{1}H, and/or ^{13}C NMR spectra to the previously reported data. Infrared spectra were recorded with a Nicolet Nexus 470 FT spectrometer. Optical rotations were measured on a Polar L-□P, IBZ Messtechnikpolarimeter at 589 nm. Elemental analyses (C, H) were performed in an EXETER CE-440 instrument at UMYMFOR (Argentina).

General Procedure For The Esterification Reactions Of (±)-BINOL (I)

A solution of (±)-BINOL (**I**), solvent, esterification agent and the corresponding carboxylic acid or acyl chloride were combined according to Methods **A** to **E**, resumed in Table 1 (see Supporting Information for complete details). The reactions were monitored by thin-layer chromatography (TLC).

Selected Data

Esterification reactions of (S)-BINOL. General Procedure for the Synthesis of enantiomerically pure (S)-1,1′-binaphthyl-2-2′-diyl dimetacrylate (IX). Method B (TFAA, H_3PO_4, r.t. or 50°C). A mixture of methacrylic acid (0.228 mL, 2.6mmol), (S)-BINOL (0.342 g, 1.2mmol) and 85% orthophosphoric acid (H_3PO_4, 0.012 mL, 0.24mmol) was stirred under **air** atmosphere. To this solution, trifluoroacetic anhydride (TFAA, 1.41 mL, 10.0mmol) was added dropwise and the resulting mixture was allowed to stir at room temperature (see Table 1). The progress of the reaction was monitored by TLC. The reaction mixture was added to a little crushed ice, extracted with diethyl ether (3 x 8 mL), washed with 10% NaOH solution (2 x 8 ml) followed by water (2 x 8 mL),

dried over anhydrous sodium sulphate and concentrated to afford the desired diester**IX**(0.507 g, quantitative yield) as a white solid, purified by recrystallization in ethanol, mp54-56°C. $[\alpha]_D^{25}$ -56.1 (c 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (6H, d, *J*= 1.1 Hz C*H*$_3$), 5.19 (2H, dd, *J*= 2.4, 1.2 Hz, C*H*$_2$), 5.54 (2H, dd, *J*= 2.4, 1.2 Hz, C*H*$_2$), 7.19 – 7.27 (4H, m, Ar-*H*), 7.31 – 7.48 (4H, m, Ar-*H*), 7.78 – 7.96 (4H, m, Ar-*H*); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 16.8, 120.7, 122.6, 124.6, 125.0, 125.6, 125.7, 126.9, 128.3, 130.4, 132.4, 134.4, 145.9, 164.3; MS (EI): m/z (relative intensity) 422.1 (M^+, 100), 284.1 (1.8), 282.1(13), 268.1 (40), 255.1 (15), 239.0 (19), 228.1 (8), 226.0 (37), 69.0 (87); Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H , 5.25. Found: C, 79.57; H, 5.20.

(S)-1,1′-binaphthyl-2-2′-diyl diacrylate (VIII): $[\alpha]_D^{25}$ -25.6 (c 1.00, $CHCl_3$); mp 71-73°C.

(S)-1,1′-binaphthyl-2-2′-diyl-(Z)-2-methyl-3-phenyl-2-propenoate (X): $[\alpha]_D^{25}$ -34.9 (c 0.95, $CHCl_3$), mp 100-102°C.

(S)-1,1′-binaphthyl-2-2′-diyl di-(Z)-2,3-diphenyl-2-propenoate (XI): [□]$_D^{25}$ -38.2 (c 0.90, $CHCl_3$); mp 90-92°C.

SUPPORTING INFORMATION

Full experimental detail, 1H and 13C spectra. This material can be found *via* the "Supplemantary Content" section of this article webpage.

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13.(a) It is important to note that compound **II** has been reported previously in very good yields but the synthesis was achieved using acetic anhydride. For further information see Kadam, S. T.; Lee, H.; Kim, S. S. TMEDA: Efficient and mild catalyst for the acylation of alcohols, phenols and thiols under solvent-free condition. *Bull. Korean Chem. Soc.* **2009**, *30*, 1071-1076; (b) Compound **III** was obtained through benzoylation under extreme conditions with benzoic anhydride and no characterization is informed. For further information seeOrita, A.;Tanahashi, C.; Kakuda, A.; Otera, J. Highly powerful and practical acylation of alcohols with acid anhydride catalyzed by $Bi(OTf)_3$. *J. Org. Chem.*

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18. Although 15-crown-5- is the specific ether to coordinate Na cation, 18-crown-6 is equally efficient and substantially cheaper.

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20. The low yield (Table 1, entry 5) could be attributed to the easily hydrolysable acetyl chloride.

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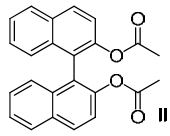
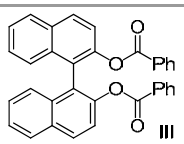
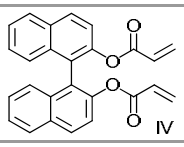
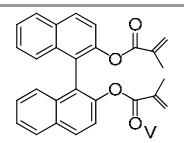
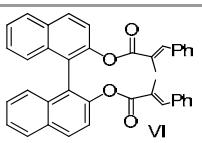
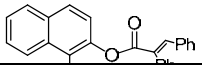
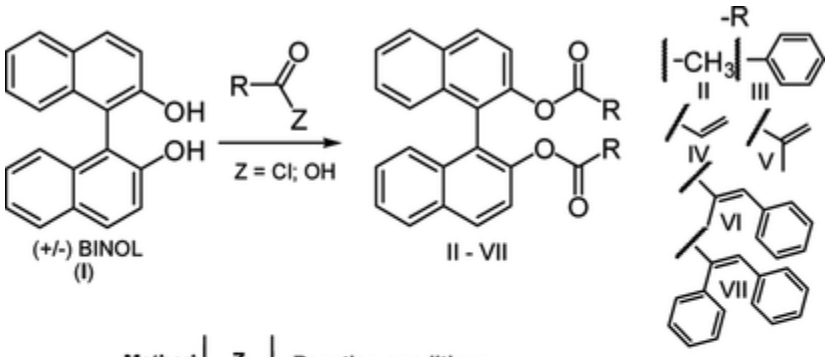
Table 1. **(±)-**BINOL diesters **II** – **VII** obtained in the esterification of (±)-BINOL (**I**) under different reaction conditions.

Entry	Acylating reagent	Reaction Conditions [a]	Time (h) [b]	Product	% Yield [c]
1	acetic acid	DCC, DMAP, $PhCH_3$,TsOH, r.t.[d]	1	 II	92.5
2		TFAA, H_3PO_4, 50°C, air atm. [e]	0.25		98
3	acetyl chloride	NaH, THF, r.t. [f]	12		75
4		NaH, THF, 18-crown-6, r.t.[g]	12		92
5		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm.[h]	24		53
6	benzoic acid	DCC, DMAP, $PhCH_3$, TsOH, r.t., [d]	2	 III	88
7		TFAA, H_3PO_4, 50°C, air atm. [e]	0.25		99
8	benzoyl chloride	NaH, THF, r.t. [f]	12		83
9		NaH, THF, 18-crown-6, r.t. [g]	8		94
10		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm. [h]	12		92
11	acrylic acid	DCC, DMAP, $PhCH_3$, TsOH, r.t. [d]	4	 IV	93
12		TFAA, H_3PO_4, r.t., air atm. [e]	0.25		100
13	acryloyl chloride	NaH, THF, r.t. [f]	--		[i]
14		NaH, THF, 18-crown-6, r.t.	12		95
15		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm. [h]	12		95
16	methacrylic acid	DCC, DMAP, $PhCH_3$, TsOH, r.t. [d]	1	 V	98
17		TFAA, H_3PO_4, r.t., air atm. [e]	0.25		100
18	methacryloyl chloride	NaH, THF, r.t. [f]	--		[i]
19		NaH, THF, 18-crown-6, r.t. [g]	12		80
20		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm. [h]	12		78
21	(Z)-2-methyl-3-phenyl-2-propenoic acid	DCC, DMAP, $PhCH_3$, TsOH, r.t. [d]	2.5	 VI	84
22		TFAA, H_3PO_4, 50°C, air atm. [e]	0.75		85
23	(Z)-2-methyl-3-phenyl-2-propenoyl chloride	NaH, THF, r.t. [f]	--		[i]
24		NaH, THF, 18-crown-6, r.t. [g]	14		67
25		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm. [h]	12		69
26	(Z)-2,3-diphenyl-propenoic acid	DCC, DMAP, $PhCH_3$, TsOH, r.t. [d]	3		81

27		TFAA, H_3PO_4, 50°C, air atm. [e]	0.75		70
28	(Z)-2,3-diphenyl-propenoyl chloride	NaH, THF, r.t. [f]	--		[i]
29		NaH, THF, 18-crown-6, r.t. [g]	12		75
30		NaOH, $Bu_4N^+Cl^-$, H_2O, CH_2Cl_2, r.t., air atm. [h]	12		80

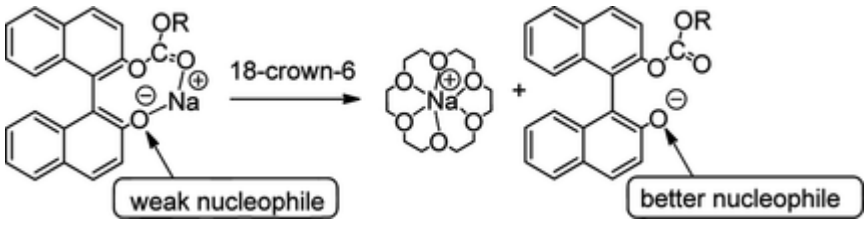
[a] Inert atmosphere of Ar unless otherwise is indicated. [b] Determined by TLC analysis. [c] Determined by CG-MS analysis of crude reaction through a standard curve generated from isolated pure product. [d] Method A. [e] Method B. [f] Method C. [g] Method D. [h] Method E. [i] Unreacted BINOL and BINOL-monoester were observed.

Scheme 1.

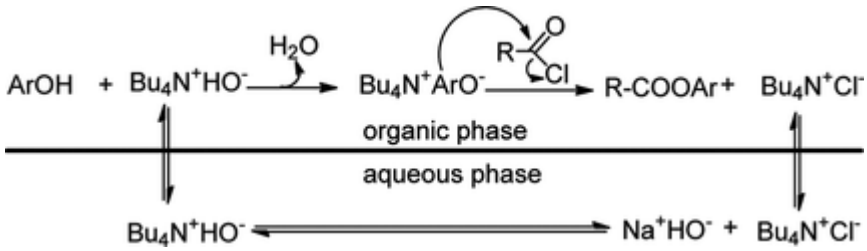


Method	Z	Reaction conditions
A	OH	DCC / DMAP / Ph-CH_3 / TsOH, r.t.
B	OH	TFAA / H_3PO_4, r.t., air atm.
C	Cl	NaH / THF, r.t.
D	Cl	NaH / THF / 18-crown-6, r.t.
E	Cl	NaOH aq. / $Bu_4N^+Cl^-$/ CH_2Cl_2, r.t., air atm.

Scheme 2.



Scheme 3.



Scheme 4.