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Synthesis of Chiral α-Diarylacetic Esters by Stereospecific 1,2-Aryl Migration Promoted by in Situ Generated Acetals from Benzoins

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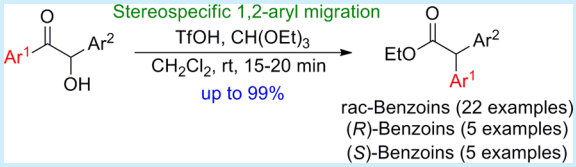
Supporting Information

ABSTRACT: A simple protocol for the synthesis of α-diarylacetic esters from benzoins is described. In situ generated acetal assists rapid 1,2-aryl migration in a stereospecific manner, paving the way to make enantioenriched α-diarylacetic esters from easily accessible enantiopure benzoins.

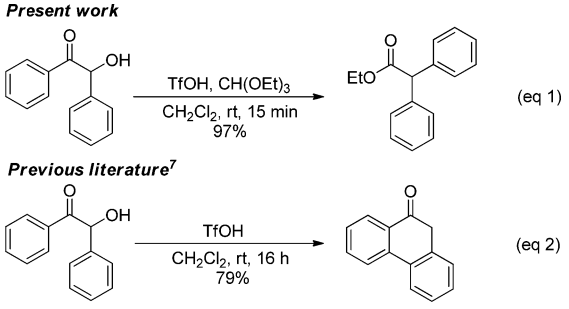


The chiral *gem*-diarylalkyl moiety is present in many pharmaceutically and biologically important compounds.[1] For example, this moiety is the key structural feature of muscarinic antagonists like fesoterodine[1b] and tolterodine (Detrol),[1c,d] antidepressants such as sertraline (Zoloft)[1e] and nomifensine,[1f] and phosphodiesterase type 4 inhibitor CDP-840.[1g] Among the chiral *gem*-diarylalkyl compounds, making enantiomerically pure α-diaryl carbonyl compounds is a really challenging task due to the associated epimerization issues. Straightforward enantioselective protonation of enolates, which is used to introduce chirality at the α-position of a carbonyl function, cannot be applied to racemic α-diaryl carbonyl compounds as it is difficult to differentiate the faces of their enolates. There are quite a few methods available for the synthesis of racemic unsymmetrical α-diaryl carbonyl compounds.[2] Several of them are based on the transition-metal-catalyzed α-arylation of α-aryl carbonyl compounds. Although the asymmetric version of transition-metal-catalyzed α-arylation[3] has seen remarkable development in recent years, it is limited to the synthesis of enantiopure α-monoaryl carbonyl compounds only.

Very few reports are available for the synthesis of enantioenriched α-diaryl carbonyl compounds.[4−6] Among them, a majorly explored strategy is the 1,2-addition of aryl boronic acids to α-ketoesters or α-diketones using chiral rhodium or ruthenium catalysts.[4] This reaction results in enantioenriched α-hydroxydiaryl carbonyl compounds. Maruoka and co-workers have developed a strategy for generating a chiral all-carbon quaternary center α to carbonyl by an interesting Brønsted acid-catalyzed insertion of aryldiazoacetate into the sp^2-carbon−CHO bond.[5] In this reaction, the chirality is transferred through (−)-phenylmenthyl auxiliary attached to the aryldiazo substrate. Davies and co-workers have reported a rhodium-catalyzed asymmetric insertion of aryl diazoacetate into the C−H bond of 1,4-cyclohexadiene and subsequent oxidation of the product using DDQ to *gem*-diarylacetates.[6] This method, however, is applicable to make enantioenriched α-diarylacetates in which one of the aryl groups is compulsorily phenyl. Herein, we report a facile strategy for obtaining racemic as well as both isomers of α-diarylacetates.

Our strategy essentially involves in situ generation of acetals from benzoins using triethyl orthoformate in the presence of TfOH and their rapid conversion into α-diarylacetates (Scheme 1, eq 1). Olah and co-workers have reported benzannulation of

Scheme 1



benzoin under the same conditions in the absence of triethyl orthoformate (Scheme 1, eq 2).[7] Thus, the 1,2-aryl migration is facilitated by the in situ formed acetal in the reactions presented in this paper. The reason is, upon 1,2-migration of aryl group, the generated carbocation is stabilized effectively by the acetal oxygen atoms. 1,2-Aryl migration has been known to provide opportunities to synthesize compounds which are difficult to make.[8] Many Lewis acids such as salts of Zn, Sn, Co, Hg, Pd, Sb, Bi, and Fe (MX_n) can promote the 1,2-aryl shift in α-haloalkylaryl acetals to α-arylalkanoic acids at reflux temperatures.[9] In these reactions, preformed acetal was employed and the affinity of metal toward halide promoted the 1,2-aryl migration. Under strong Brønsted/Lewis acidic conditions, it is known that aldehydes and ketones are converted in to corresponding acetals in the presence of trialkyl orthoformates.[10] Miroslav and co-workers have used in situ formed acetal for the preparation of methyl 2-(4-ethylphenyl)-2-methylpropionate from 1-(4-ethylphenyl)-2-hydroxy-2-methylpropan-1-one.[9a] However, synthesis of enantioenriched *gem*-

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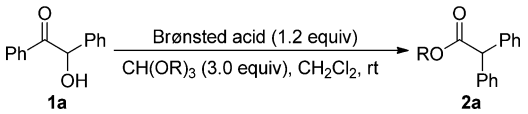
diarylacetates have not been explored in the above-mentioned reactions involving 1,2-aryl migration.

Optimization of reaction conditions was carried out using different Brønsted acids taking benzoin as the starting material. Table 1 summarizes the results of these reactions. Among the

Table 1. Screening of Different Brønsted Acids in the Conversion of Benzoin into Diphenylacetate Derivatives



1a 2a

entry	Brønsted acid	R	time	yield[a] (%)
1	CH_3SO_3H	Et	1 h	89
2	TFA	Et	24 h	79
3	PTSA	Et	24 h	70
4	$HClO_4$	Et	24 h	11
5	(+)-CSA	Et	24 h	49
6	HCl	Et	24 h	trace
7	Amberlyst 15	Et	24 h	NR
8	Amberlite IR 120	Et	24 h	NR
9	**TfOH**	**Et**	**15 min**	**97**
10	TfOH	Me	15 min	95
11	TfOH[b]	Me	4 h	6
12	TfOH[c]	Me	27 h	61

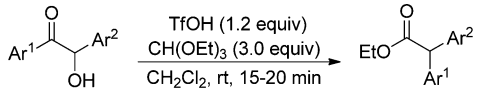
[a]Isolated yield. [b]10 mol %. [c]50 mol %. NR: no reaction.

Brønsted acids studied, triflic acid was found to be the best in the presence of 3 equiv of triethyl orthoformate, and the reaction was complete in 15 min at room temperature (Table 1, entry 9). With substoichiometric amount of triflic acid the reaction resulted in poor yields of the product (Table 1, entries 11 and 12).

The optimized reaction conditions (Table 1, entry 9) were employed in the 1,2-aryl migration reactions of different benzoins. The results are presented in Table 2. Benzoins employed in this study were prepared either by trivial benzoin condensation or a two-step process involving (2-aryl-1,3-dithan-2-yl)lithium addition to arylaldehydes followed by deprotection of dithiane moiety.[11] Benzoins having different substituents like F, Cl, Br, Me, OMe, OCH_2O, OTBDPS, OTBDMS, OH, and OAc on aryl rings were employed. The reactions were fast and completed in less than 20 min. The reactions were clean and the yields were generally excellent. To extend this methodology, 1,2-alkyl migration was probed using the substrates 1-hydroxy-1-phenylpentan-2-one (**1w**)[11] and 1-hydroxy-3-methyl-1-phenylbutan-2-one (**1x**).[11] Unfortunately, both reactions resulted in complex reaction mixtures.

We then focused our attention on the synthesis of enantiomerically pure benzoins to check whether the 1,2-aryl migration in the present reaction occurs at the same time as the OH leaves in the form of water. For the synthesis of optically pure benzoins a new protocol was designed. The benzylic alcohol derivatives obtained in the reaction of (2-aryl-1,3-dithan-2-yl)lithium with arylaldehydes were oxidized to their corresponding ketones. CBS reduction was carried out on the ketone function and deprotection of dithiane in the resulting alcohols generated optically active benzoins with high enantiomeric purities.[11] This way, both isomers of benzoins could be obtained using (*S*)-DPP and (*R*)-DPP in high ee.[12] This new protocol for the synthesis of enantiopure benzoins is very straightforward. Enantioselective CBS reduction of 2-acyl-

Table 2. Scope of in Situ Formed Acetal-Assisted 1,2-Aryl Migration



1a-1v 2a-2v

entry	1	Ar^1	Ar^2	2	yield[a] (%)
1	**1a**	Ph	Ph	**2a**	97
2	**1b**	$4\text{-}FC_6H_4$	$4\text{-}FC_6H_4$	**2b**	90
3	**1c**	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	**2c**	88
4	**1d**	$4\text{-}BrC_6H_4$	$4\text{-}BrC_6H_4$	**2d**	78
5	**1e**	Ph	$2\text{-}ClC_6H_4$	**2e**	98
6	**1f**	Ph	$4\text{-}ClC_6H_4$	**2f**	97
7	**1g**	Ph	$2,4\text{-}Cl_2C_6H_3$	**2g**	80
8	**1h**	$4\text{-}MeC_6H_4$	Ph	**2h**	99
9	**1i**	$4\text{-}MeC_6H_4$	$4\text{-}ClC_6H_4$	**2i**	95
10	**1j**	$4\text{-}MeC_6H_4$	$3\text{-}FC_6H_4$	**2j**	97
11	**1k**	$4\text{-}(OMe)C_6H_4$	$4\text{-}ClC_6H_4$	**2k**	87
12	**1l**	$4\text{-}(OMe)C_6H_4$	$4\text{-}FC_6H_4$	**2l**	92
13	**1m**	$4\text{-}ClC_6H_4$	$4\text{-}FC_6H_4$	**2m**	90
14	**1n**	$3,4\text{-}(OMe)_2C_6H_3$	Ph	**2n**	83
15	**1o**	$3,4\text{-}(OMe)_2C_6H_3$	$4\text{-}ClC_6H_4$	**2o**	95
16	**1p**	$3,4\text{-}(OCH_2O)C_6H_3$	Ph	**2p**	98
17	**1q**	$3,4\text{-}(OCH_2O)C_6H_3$	$4\text{-}FC_6H_4$	**2q**	88
18	**1r**	$3,4\text{-}(OCH_2O)C_6H_3$	$4\text{-}ClC_6H_4$	**2r**	91
19	**1s**	$4\text{-}(TBDPSO)C_6H_4$	C_6H_5	**2s**	86
20	**1t**	$4\text{-}(TBDMSO)C_6H_4$	C_6H_5	**2t**	90
21	**1u**	$4\text{-}(OH)C_6H_4$	C_6H_5	**2u**	76
22	**1v**	$4\text{-}(OAc)C_6H_4$	C_6H_5	**2v**	85

[a]Isolated yield.

1,3-dithianes using B-Ph oxazaborolidine derivative as the catalyst has been reported to show good enantioselectivities.[13] In these substrates, the bulkiness is imparted by the dithiane moiety and good enantioselectivities were obtained only when the acyl group is kept less bulky like acetyl. When the acyl group is propanoyl the enantioselectivity reduced considerably. However, using classical B-Me oxazaborolidine as catalyst, we were delighted to observe very good enantioselectivities with our substrates having bulky aryloyl as the acyl component. Benzoins (*R*)-**1f**, (*R*)-**1l**, and (*S*)-**1l** have already been reported. By analogy, the absolute configurations of other benzoins were assigned.

Both (*R*)- and (*S*)-benzoins were subjected to in situ formed acetal-assisted 1,2-aryl migration separately. Interestingly, the aryl migration took place in a stereospecific way to result in enantioenriched ethyl α-diarylacetates in excellent yields (Tables 3 and 4). That is, the aryl migration took place from back side of the leaving OH group in a concerted process.[14] The anchimeric assistance of aryl group and stabilization of carbocationic center by acetal function favor this stereospecific 1,2-aryl migration. Except in the reaction of (*S*)-**1m**, the ee of the products are the same or slightly less than that of the starting benzoins. Whenever there was an electron-withdrawing fluoro substituent present in the aryl ring, the ee was slightly reduced. This effect was greater with substrate **1m**, which contains *p*-F-phenyl and *p*-Cl-phenyl groups.

In summary, a simple protocol involving in situ generated acetal-assisted 1,2-aryl migration for the synthesis of *gem*-diarylacetates has been developed. Using this method, enantioenriched α-diarylacetates which are otherwise difficult to make could be prepared from easily accessible enantiomeri-

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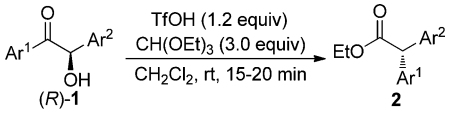
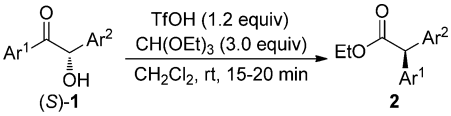
Table 3. Preparation of Enantiopure α-Diarylacetic Esters from (*R*)-Benzoins



entry	1	ee (%)	2	yield[a] (%)	ee (%)
1	(*R*)-**1f**	91	(*S*)-**2f**	87	88
2	(*R*)-**1k**	87	(*S*)-**2k**	90	87
3	(*R*)-**1l**	92	(*S*)-**2l**	88	90
4	(*R*)-**1q**	98	(*R*)-**2q**	87	93
5	(*R*)-**1r**	95	(*R*)-**2r**	88	93

[a]Isolated yield.

Table 4. Preparation of Enantiopure α-Diarylacetic Esters from (*S*)-Benzoins



entry	1	ee (%)	2	yield[a] (%)	ee (%)
1	(*S*)-**1f**	99	(*R*)-**2f**	96	93
2	(*S*)-**1l**	96	(*R*)-**2l**	93	91
3	(*S*)-**1m**	99	(*S*)-**2m**	93	85
4	(*S*)-**1q**	98	(*S*)-**2q**	96	92
5	(*S*)-**1r**	97	(*S*)-**2r**	85	96

[a]Isolated yield.

cally pure benzoins. Optically active α-diarylacetates could serve as valuable building blocks for the synthesis of interesting molecular skeletons.

■ ASSOCIATED CONTENT

Supporting Information

Complete experimental details, HPLC traces of enantiopure compounds, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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