



Dual behavior of alcohols in iodine-catalyzed esterification under solvent-free reaction conditions

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ABSTRACT

The dual behavior phenomenon of alcohols in iodine-catalyzed esterification under solvent-free reaction conditions (SFRCs) is described; the governing factor is the stability of the carbonium ion generated from the alcohol; high concentration reaction conditions (HCRCs) or dilute solutions are much less suitable. In the case of benzylic alcohols, loss of optical activity was noted, whereas alkyl alcohols furnished a product with retention of stereochemistry.

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1. Introduction

Important tasks of modern chemistry are preservation of the environment and the development of new methods and technologies.¹ One of the important strategies is performing reactions without the use of a solvent.² However, transformations under solvent-free reaction conditions (SFRCs) can undergo a different scenario, while heat exchange is very important particularly in exothermic reactions.³ Recently, the important role of a small amount of solvent in solid-state reactions and reactions under highly concentrated conditions was established.⁴ Esterification is an important transformation in organic chemistry,⁵ and several different approaches for this reaction have been developed.⁶ More reactive precursors can be employed for esterification, but acids and alcohols in conjunction with a Lewis catalyst are still primarily used.⁷ A Lewis catalyst could activate either the alcohol or acid depending on its structure, which is finally reflected in the stereochemistry of the reaction product. However, the principal drawbacks of the majority of Lewis catalysts are moisture-sensitivity, high cost, and toxicity. Many esterification methods require azeotropic removal of water, or at least the presence of a drying agent. Iodine is a versatile and mild Lewis catalyst for the activation of alcohols and acids.⁸ Recently, research was published describing iodine-catalyzed esterification with a large excess of alcohol at an elevated temperature and this method appears to be highly water tolerant.⁹ We have already shown that alcohols can be transformed into al-

kenes and further into indane derivatives in the presence of iodine under SFRC.¹⁰ We have also demonstrated that iodine is able to discriminate between H₂O, MeOH, and H₂O₂ and, on the other hand, between OH, OMe, and OOH groups.¹¹ In order to clarify the role of iodine in the transformation of alcohols in the presence of acids under SFRC, the dual behavior of alcohols in esterification reactions is described in this Letter.

Initially, the esterification of cyclohexanol with acetic acid at 85 °C in a 1:1 molar ratio with and without I₂ was studied. After 2.5 h, only trace amounts of ester were detected without I₂; in the presence of iodine (3 mol %) a conversion of 61% was achieved. The reaction could be further accelerated (85% conversion) using a twofold molar excess of acid, indicating that a much lower excess was necessary than that mentioned in studies already published.⁹ Encouraged with this finding, we studied the effect of the structure of the alcohol on the course of the esterification (Table 1). It is evident that pentanol **1a** and hexadecanol **1b** could be readily esterified in high yields (entries 1 and 2). It is known that the ring size of cycloalkanols plays an important role when the formation of carbocationic intermediates is the main reaction route. Cyclopentanol was the most reactive and the reactivity of the cycloalkanols decreased slightly with increased ring size (entries 3, 5, 7, and 9); alcohols **1c–f** were converted efficiently to the corresponding esters (entries 4, 6, 8, and 10).

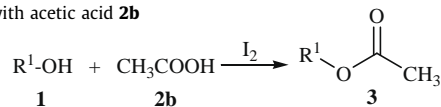
Interestingly, HCOOH (3 equiv) reacted efficiently (85–96%) with alcohols **1a–f** without I₂, while in the presence of I₂ up to 5% higher conversion was achieved. Next, we evaluated the role of water in the iodine-catalyzed esterification of cyclooctanol and, as seen in Figure 1, the conversion decreased from 86% to 44% as the water content increased (up to 9 mmol).

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Table 1
The role of alcohol **1** in the iodine-induced esterification with acetic acid **2b**



Entry	Alcohol	1	Reaction conditions ^a	3	Conversion ^b (%)
1	CH ₃ (CH ₂) ₃ CH ₂ OH	a	A / 2.5 h	ab	88 (74)
2	CH ₃ (CH ₂) ₁₄ CH ₂ OH	b	A / 2.5 h	bb	93 (85)
3		c	B / 0.5 h	cb	61
4		c	A / 2.5 h	cb	89 (68)
5		d	B / 0.5 h	db	50
6		d	A / 2.5 h	db	85 (70)
7		e	B / 0.5 h	eb	44
8		e	A / 2.5 h	eb	86 (71)
9		f	B / 0.5 h	fb	45
10		f	A / 2.5 h	fb	85 (71)

^a 1 mmol of **1**, (A) 3 mmol of **2b**; (B) 1 mmol of **2b** and 0.03 mmol of I₂, 85 °C.

^b Conversion determined by ¹H NMR, values in parentheses refer to isolated yields.

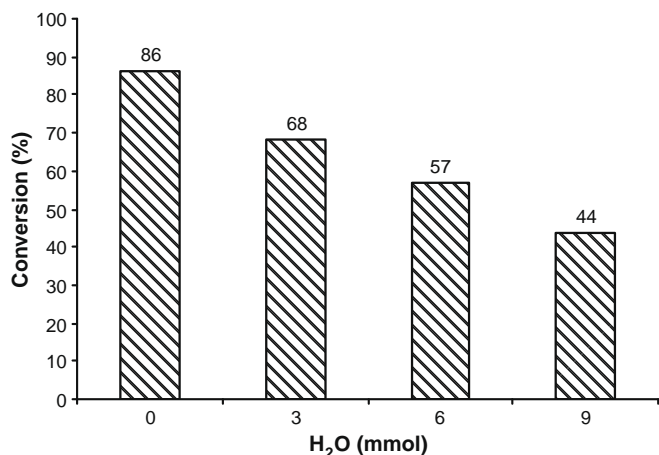


Figure 1. The effect of the amount of water on the iodine (0.03 mmol) induced esterification of cyclooctanol (**1f**, 1 mmol) with CH₃COOH (3 mmol) (*T* = 85 °C, 2.5 h).

The transformation is suppressed to a significant extent, but somewhat less than might be expected for a reversible reaction. The role of water was examined further in the reaction of **1d/2b**, (1:1) where the drying agent Na₂SO₄ was added (40, 60, and 80 mol %). This brought no advantage, which however, means that the water formed did not shift the equilibrium toward the reactants.

From the above experiments it is evident that the acid is more likely to be activated than the alcohol. Thus, the esterification of alcohols where a stereochemical outcome and a potential rearrangement would be indicators of carbocationic intermediates were examined (Table 2). Firstly, a mixture of *trans/cis* (66:34) 4-*tert*-butylcyclohexanol **4a** was reacted with CH₃COOH and a mixture of esters **5a** was formed in almost the same ratio (67:33). This indicates that activation of **4a** did not take place and the involvement of carbocations is less likely. Additionally, it was discovered that the *trans* alcohol was more reactive than the *cis* stereoisomer. Conversion of **4a** after 14 h at 85 °C was 68%, while the *trans/cis* ratio of acetate **5a** was altered to 71:29 in favor of the *trans* isomer. 2-Adamantanol **4b** was esterified to **5b** without any rearrangement. Norbornene derivatives are very sensitive to the Meerwein–Wagner rearrangement and hydride shifts when cationic species are intermediates. However, no rearrangement took place and **5c** and **5d** were the exclusive products. Finally, the optically pure menthol enantiomers **4e** and **4f** were esterified with

CH₃COOH. The sole product in each case was the acetate ester with complete retention of configuration.

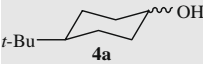
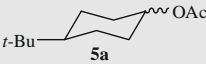
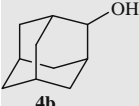
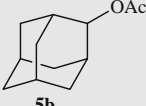

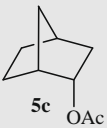
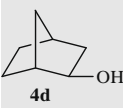
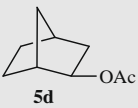
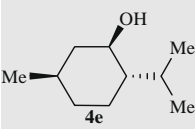
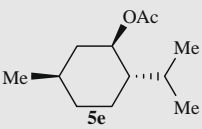
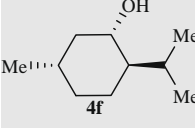
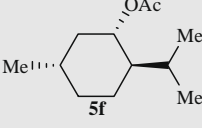
All these examples favor activation of the acid or both reactants and are against the formation of carbocationic intermediates. Norbornenol is known to undergo esterification with HCOOH when used in large excess,¹² however, **4c** and **4d** furnished the expected formate esters in 93–94% yields with 3 equiv of HCOOH. Alcohols **4a** and **4e** gave formate analogues in 67% and 69% conversion without I₂, and in 89% and 95% conversion in the presence of I₂. In addition, we investigated the effect of the amount of acid on the conversion of (–)-menthol (Fig. 2). After 7 h, using 1 equiv of CH₃COOH, we achieved 65% conversion, however, the conversion rose to 83% when using 3 equiv of CH₃COOH.

Introduction of a phenyl ring to a saturated carbon atom enhances the stability of carbonium ions when formed.

Consequently, we investigated both the electronic and steric stabilizing effects on benzyl alcohol **6a** and 1-phenylethanol **6b** (Scheme 1 and Table 3). Both alcohols reacted readily (85% and 74% conversion) with HCOOH without I₂, but conversion in the presence of I₂ was higher (entries 1 and 5). Acetic acid is less reactive than formic acid, whilst octanoic and benzoic acids are far less reactive (entries 2–4). A careful analysis of the crude reaction mixture revealed the presence of another type of product, namely dibenzyl ether **7a** (entry 3), which was a major product in the case of benzoic acid (entry 4). Alcohol **6b** is less reactive than **6a**, and 85% conversion into **8ba** was achieved after 6 h, with only a small amount of ether **7b** being formed; its amount increased with longer reaction times (entries 6 and 7). Propionic acid is a little less reactive than acetic acid, as reflected in the higher dimer proportion, similar to octanoic acid (entries 7–12). The reactivity of branched and sterically hindered and solid acids is still lower and the amount of **7b** is increased (entries 13–18). Finally, the stereochemical outcome was tested utilizing (*S*)-Mosher's acid and the same result was obtained regardless of the absolute configuration of 1-phenylethanol. An equimolar mixture of diastereoisomeric esters was formed accompanied by small amounts of **7b** (entries 19–21). This result strongly suggests that iodine activates the alcohol, thus forming a cationic intermediate which consequently leads to a loss of the stereochemical integrity.

Introduction of a methoxy group to the phenyl ring can influence substantially the reaction course, particularly if cationic intermediates are implicated. The reaction pathways are depicted in Scheme 1. Indeed, 4-methoxybenzyl alcohol **6e** exhibited the most complex behavior in this study; it is much more reactive than **6a**, yet dimerization of **6e** is more pronounced, and in addition *ipso*-substitution also occurred without I₂ (Table 4, entry 1).

Table 2
The effect of the structure of alcohol **4** on the stereochemistry of esterifications with acetic acid **2b** induced by iodine

Alcohol	Ester	Reaction time ^a (h)	Conversion ^b (%)
 4a Trans/cis = 1.9	 5a Trans/cis = 2.0	24	78 (70)
 4b	 5b	5	92 (75)
 4c	 5c	2.5	87 (72)
 4d	 5d	2.5	86 (69)
 4e	 5e	7	83 (78)
 4f	 5f	7	85 (81)

^a Reaction conditions: 1 mmol of **4**, 3 mmol of **2b**, and 0.03 mmol of I₂, 85 °C.

^b Conversion determined by ¹H NMR, values in parentheses refer to isolated yields.

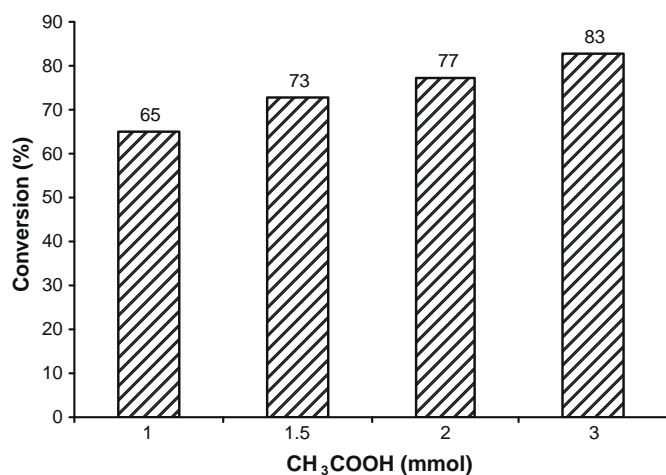
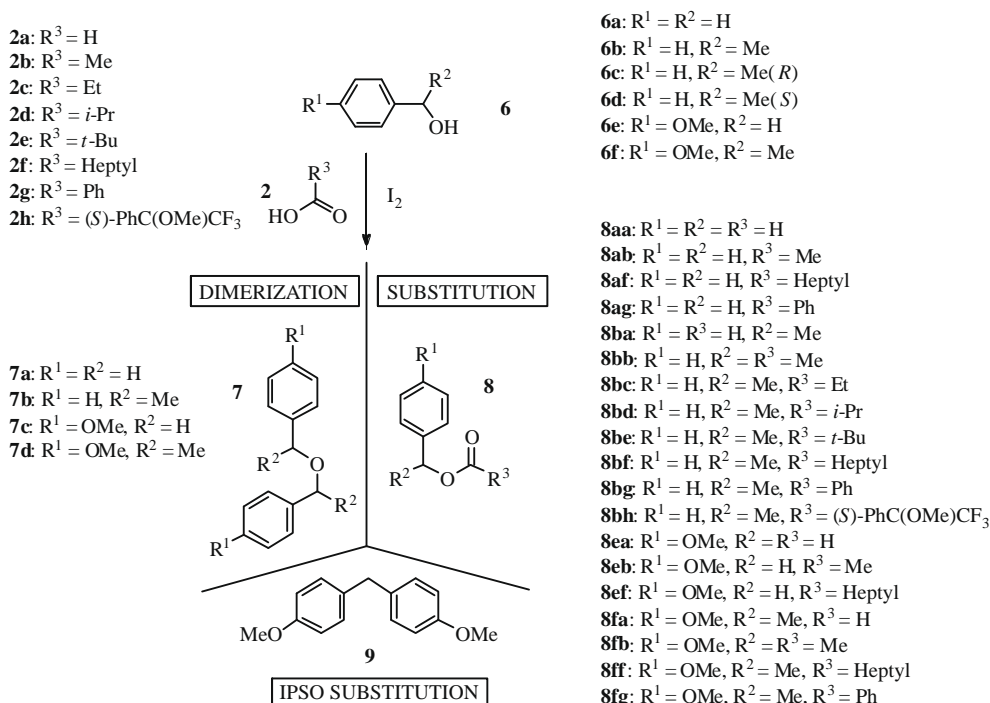


Figure 2. The effect of amount of acetic acid **2b** on the iodine (0.03 mmol) induced esterification of (–)-menthol (**4e**, 1 mmol, 85 °C, 7 h).

Both alcohols **6a** and **6e** reacted well (85% and 89%) with HCOOH without I₂, whereas the distribution of the products varied only slightly from the catalyzed reaction. The proportion of ester

decreased with the diminishing reactivity of the acid; concomitantly, the latter two processes became more pronounced (entries 2 and 3). In the case of benzoic acid, the dimer **7c** was the major product along with **9**, however, no ester was formed (entry 4). In a separate experiment it was established that **9** was not formed from **7c** and benzoic acid in the presence of I₂. 1-(4-Methoxyphenyl)ethanol **6f** possesses a higher reactivity than **6e**; high conversions were readily achieved at rt with all the acids tested (entries 5–8). The highest proportion of dimer **7d** was obtained with benzoic acid (entry 8), while no *ipso*-substitution took place. In an independent experiment, dimer **7d** was reacted with HCOOH in the absence of I₂ and 77% conversion to the formate ester was noted, 4% of 1-(4-methoxyphenyl)ethanol was also formed. In addition, the role of the amount of acid and its structure on the esterification of cyclohexanol **1d** was investigated (Table 5). It is evident that the molar ratio is an essential factor in terms of the reaction progress. The reactivity of the acids decreases with lengthening of the alkyl chain and with branching.

The role of the reaction conditions (SFRCs vs high concentration reaction conditions HCRCs) and the role of iodine on esterification reactions were examined (Table 6). It is evident that formic acid, in contrast to acetic acid, reacts to a significant extent with all three alcohols without iodine, confirming the important role of pK_a (entries 3, 9, and 15). The concentration of reactants was found to be of paramount importance; the highest conversions were achieved



Scheme 1. Reaction pathways of benzylic alcohols in I₂-catalyzed esterification under SFRC.

Table 3

The effect of carboxylic acid **2** and phenyl substituted alcohol **6** on iodine-induced transformations

Entry	Alcohol		Acid	Reaction conditions ^a	Conv. (%)	Subst./Dim. 8:7
	6	R ²				
1	a	H	H	3 h / 25 °C	92	100
2	a	H	Me	24 h / 55 °C	87	100
3	a	H	Heptyl	74 h / 85 °C	88	91:9
4	a	H	Ph	192 h / 55 °C	86	44:56
5	b	Me	H	6 h / 25 °C	85	98:2
6	b	Me	H	144 h / 25 °C	89	89:11
7	b	Me	Me	20 h / 25 °C	46	74:26
8	b	Me	Me	144 h / 25 °C	84	81:19
9	b	Me	Me	17 h / 55 °C	82	80:20
10	b	Me	Et	20 h / 25 °C	43	50:50
11	b	Me	Et	144 h / 25 °C	81	69:31
12	b	Me	Heptyl	72 h / 55 °C	81	68:32
13	b	Me	<i>i</i> -Pr	20 h / 25 °C	31	32:68
14	b	Me	<i>i</i> -Pr	144 h / 25 °C	75	50:50
15	b	Me	<i>t</i> -Bu	20 h / 25 °C	15	17:83
16	b	Me	<i>t</i> -Bu	144 h / 25 °C	72	26:74
17	b	Me	<i>t</i> -Bu	72 h / 55 °C	77	48:52
18	b	Me	Ph	22 h / 55 °C	84	43:57
19	c	Me	M. A. ^b	166 h / 25 °C	88	94:6
20	c	Me	M. A. ^b	166 h / 25 °C	88	97 ^c :3
21	d	Me	M. A. ^b	166 h / 25 °C	90	97 ^c :3

Subst. = substitution; Dim. = dimerization.

^a 1 mmol of **6**, 3 mmol of **2**, and 0.03 mmol of I₂.

^b M. A. = Mosher's acid: (*S*)-(-)- α -methoxy- α -trifluoromethylphenylacetic acid.

^c Equimolar mixture of diastereoisomeric esters.

under SFRC, reactions in CH₂Cl₂ under HCRCs were considerably retarded (entries 1, 2, 7, and 8), while only a minor suppression was noted in the case of **6f** (entries 13 and 14). Reactivity under SFRC is still unpredictable, HCOOH in many cases reacts without a catalyst, exhibiting acidity that is a crucial parameter in combination with SFRC.

In conclusion, we have demonstrated that iodine is an efficient dual role catalyst for esterification under solvent-free reaction conditions, which are superior to dilute and high concentration reac-

tion conditions. Water has a surprisingly modest deteriorating influence on the reaction. Formic acid exhibited the highest reactivity among the tested acids since it reacted without iodine; longer chain aliphatic and branched chain acids were less reactive, signifying the influence of pK_a. The aliphatic alcohols, utilized as stereochemical probe yielded esters with retention of stereochemistry, indicating that activation of the acid or both reactants takes place. Loss of stereochemical integrity was observed in the case of both chiral 1-phenylethanol suggesting carbocationic intermediates. Three types of transformation were established: esterification, dimerization of the starting alcohol and *ipso*-substitution in the case of 4-methoxybenzyl alcohol. Primary and secondary benzylic alcohols are more reactive than aliphatic alcohols, whilst the introduction of a methoxy group enhanced their reactivity.

Typical experimental procedure: To a stirred mixture of alcohol (1 mmol) and acid (3 mmol), I₂ (0.03 mmol) was added. The reaction mixture was stirred at an appropriate temperature (reaction temperature, 55 °C or 85 °C) until TLC showed complete or at least high conversion of the starting material. The mixture was cooled to room temperature, diluted with *tert*-butyl methyl ether, washed with aqueous Na₂S₂O₃, NaHCO₃, and water and dried over anhydrous Na₂SO₄. The solution was filtered and the solvent removed under reduced pressure. The crude reaction mixture was subjected to column chromatography using hexane or petroleum ether/*tert*-butyl methyl ether mixtures and pure product(s) were obtained.

2. Spectral data of selected compounds

2.1. 4-Methoxybenzyl octanoate **8ef**

Column chromatography (SiO₂, petroleum ether/*tert*-butyl methyl ether (15:1) and preparative TLC [SiO₂, (petroleum ether/*tert*-butyl methyl ether (97:3)], yield 42%, colorless oil, ¹H NMR (CDCl₃, 300 MHz): δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.14–1.38 (m, 8H), 1.49–1.70 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 5.04 (s, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 14.0, 22.6, 25.0, 28.9, 29.1, 31.6, 34.4, 55.3, 65.9,

Table 4The role of a methoxy substituent on the phenyl ring of alcohol **6** and carboxylic acid structure **2** on iodine-induced transformations

Entry	6	R ³	Reaction conditions ^a	Conversion (%)	Subst./Dim./Ipsos 8:7:9
1	6e	H	0.67 h / 25 °C	100	74:13:13
2	6e	Me	3 h / 55 °C	98	75:2:23
3	6e	Heptyl	5 h / 55 °C	92	63:11:26
4	6e	Ph	1 h / 25 °C	61	68:32
5	6f	H	0.5 h / 25 °C	100	90:10
6	6f	Me	6 h / 25 °C	96	67:33
7	6f	Heptyl	6 h / 25 °C	85	79:21
8	6f	Ph	6 h / 25 °C	92	37:63

^a 1 mmol of **6**, 3 mmol of **2**, and 0.03 mmol of I₂.**Table 5**The role of the structure of acid **2** on the iodine-induced esterification of cyclohexanol **1d**

Acid R ³ COOH	Ratio	Reaction time ^a (h)	3	Conversion ^b (%)
R ³	2	1d:2		
Me	b	1:1	2.5	db 61
Me	b	1:2	2.5	db 78
Me	b	1:3	2.5	db 85 (70)
Et	c	1:3	2.5	dc 86 (75)
<i>i</i> -Pr	d	1:3	6	dd 84 (77)
<i>t</i> -Bu	e	1:3	120	de 83 (60)

^a 1 mmol of **1d**, 1–3 mmol of **2**, and 0.03 mmol of I₂, 85 °C.^b Conversion determined by ¹H NMR, values in parentheses refer to isolated yields.

113.9, 128.3, 130.0, 159.6, 173.8. IR (neat): 2929, 2856, 1736, 1614, 1514, 1462, 1249, 1162, 1109, 1036, 822 cm⁻¹. Anal. Calcd for C₁₆H₂₄O₃: C, 72.69; H, 9.15. Found: C, 72.83; H, 9.41.

2.2. (±)-(4-Methoxyphenyl)ethyl benzoate **8fg**

Column chromatography (SiO₂, *tert*-butyl methyl ether), yield 20%, viscous colorless oil, ¹H NMR (CDCl₃, 300 MHz): δ 1.66 (d, *J* = 6.6 Hz, 3H), 3.79 (s, 3H), 6.09 (q, *J* = 6.6 Hz, 1H), 6.87 (d,

J = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.40–7.46 (m, 2H), 7.48–7.56 (m, 1H), 8.01–8.07 (m, 2H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 22.1, 55.2, 72.6, 113.9, 127.5, 128.3, 129.6, 130.6, 132.8, 133.8, 159.3, 165.8. *m/z* (EI): 256 (M⁺, 30%), 135 (100), 105 (49), 77 (32). HRMS calcd for C₁₆H₁₆O₃ 256.1099, found 256.1103. IR (neat): 2978, 2934, 2836, 1715, 1611, 1515, 1451, 1269, 1248, 1176, 1111, 1062, 1032, 831, 712 cm⁻¹.

2.3. Bis(1-phenylethyl) ether **7b**

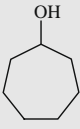
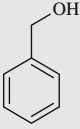
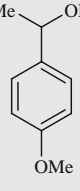
Column chromatography (SiO₂, hexane), yield 81%, colorless oil (a mixture of diastereoisomers), ¹H NMR (CDCl₃, 300 MHz): δ 1.35 (*J* = 6.5 Hz, 6H) (major isomer), 1.44 (d, *J* = 6.4 Hz, 6H), 4.19 (q, *J* = 6.5 Hz, 2H) (major isomer), 4.49 (q, *J* = 6.4 Hz, 2H), 7.02–7.37 (m, 20H). *m/z* (EI): 211 (M⁺–Me, 4%), 121 (15), 105 (100). IR (neat): 3061, 3029, 2974, 2928, 2880, 1491, 1449, 1368, 1205, 1091, 1029, 948, 760, 700 cm⁻¹.

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Table 6

The effect of reaction conditions, alcohol and acid structure on transformations: SFRC vs solution

Alcohol	Entry	Acid	I ₂ (%)	Reaction conditions ^a	Reaction time (h)	Conversion. (%)
	1	2a	0	A	6	27
	2	2a	0	B	6	13
	3	2a	0	SFRC	6	88
	4	2a	3	SFRC	6	94
	5	2b ^b	0	SFRC	2.5	9
	6	2b ^b	3	SFRC	2.5	86
	7	2a	0	A	3	13
	8	2a	0	B	3	7
	9	2a	0	SFRC	3	85
	10	2a	3	SFRC	3	92
	11	2b ^c	0	SFRC	24	15
	12	2b ^c	3	SFRC	24	87
	13	2a	0	A	0.5	80
	14	2a	0	B	0.5	60
	15	2a	0	SFRC	0.5	89
	16	2a	3	SFRC	0.5	100
	17	2b	0	SFRC	6	8
	18	2b	3	SFRC	6	96

^a 1 mmol of alcohol, 3 mmol of acid with or without 0.03 mmol of iodine: SFRC or addition of CH₂Cl₂: A—1 mL, B—2 mL at 25 °C.^b 85 °C.^c 55 °C.

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References and notes

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