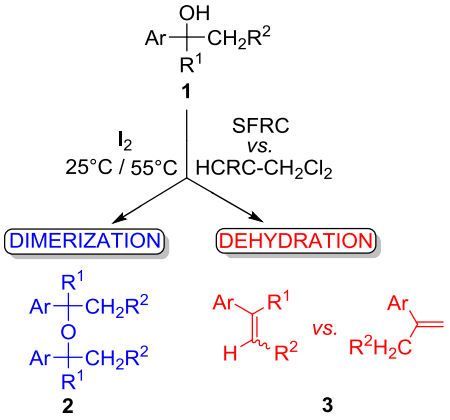


	Ar	R^1	R^2
1a	Ph	H	H
1b	Ph	H	Ph
1c	Ph	CH_3	Ph
1d	Ph	Ph	H
1e	Ph	Ph	CH_3
1f	Ph	Ph	Br
1g	Ph	Ph	F
1h	*p*-An	H	H
1i	*p*-An	H	Ph
1j	*p*-An	Ph	H
1k	*o*-An	Ph	H
1l	*p*-An	*p*-An	Ph

p-An = 4-MeO-C_6H_4 *o*-An = 2-MeO-C_6H_4

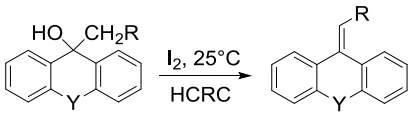
Scheme 1. The reaction pathways of the aryl-substituted alcohols in I_2-catalyzed reaction.

Table 1. The effect of the alcohol structure **1** and reaction conditions (SFRC *vs*. HCRC) on the type of iodine-induced transformation

Entry	Alcohol				Reaction conditions[a] and time	Conversion[b] [%]	Dimerization / Dehydration	
	Ar	R^1	R^2	**1**			**2**	**3**
1	Ph	H	H	**a**	A, 165 h	38	100	
2					B, 165 h	90	100	
3	Ph	H	Ph	**b**	A, 67 h	88	81	19
4					B, 67 h	10	100	
5	Ph	CH_3	Ph	**c**	A, 20 h	100		100[c]
6					B, 48 h	100		100[d]
7	Ph	Ph	H	**d**	A, 10 min	100		100
8					B, 1 h	97		100
9	Ph	Ph	CH_3	**e**	A, 3 h[e]	100		100
10					B, 1 h	10		100
11	Ph	Ph	Br	**f**	A, 96 h[e]	98		100
12					B, 1 h	0		
13	Ph	Ph	F	**g**	A, 192 h[e]	57		100
14					B, 1 h	0		
15	*p*-An	H	H	**h**	A, 15 min	92	100	
16					B, 15 min	92	100	
17	*p*-An	H	Ph	**i**	A, 230 min	100	73	27
18					B, 1 h	95	100	
19	*p*-An	Ph	H	**j**	A, 5 min	100		100
20					B, 5 min	100		100
21	*o*-An	Ph	H	**k**	A, 15 min	100		100
22					B, 15 min	100		100
23	*p*-An	*p*-An	Ph	**l**	A, 200 min	31		100
24					B, 200 min	100		100

[a] A: SFRC; 1 mmol of **1** and 0.03 mmol of I_2; B: HCRC; 1 mmol of **1**, 3 mmol of CH_2Cl_2 and 0.03 mmol of I_2. [b] Conversion and product distribution determined by ^{1}H NMR spectroscopy. [c] 4% of (*Z*)-isomer relatively to (*E*)-alkene, traces of the Hofmann alkene. [d] 5% of (*Z*)-isomer relatively to (*E*)-alkene, Zaitsev *vs*. Hofmann = 85/15. [e] Reaction temperature was 55 °C, in all other cases was 25 °C.

Table 2. The effects of geometry, ring size and substituents on the iodine-catalyzed dehydration of tertiary alcohols **4**

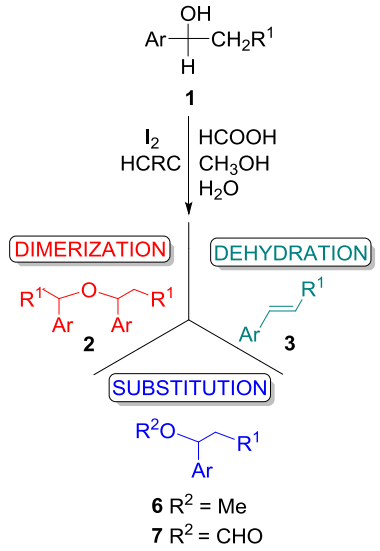


4 **5**

Entry	Alcohol			Reaction time[a]	Conversion [%][b]
	Y	**R**	**4**		
1	Ø	CH_3	**a**	15 min	3
2				23 h	100
3	Ø	Ph	**b**	15 min	0
4				96 h	0
5	CH_2CH_2	CH_3	**c**	15 min	79
6				154 min	100
7	CH_2CH_2	Ph	**d**	15 min	35
8				154 min	100
9	O	CH_3	**e**	15 min	67
10				60 min	100
11	O	Ph	**f**	15 min	65
12				30 min	100

[a] Reaction conditions: 1 mmol of **4**, 3 mmol of CH_2Cl_2 and 0.03 mmol of I_2 stirred at 25 °C, R. t. (reaction time). [b] Determined by ^{1}H NMR spectroscopy.

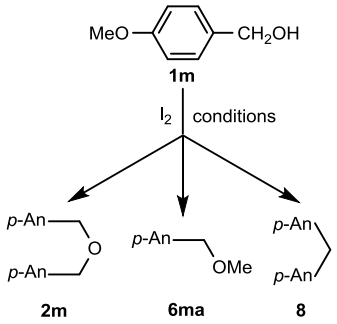
Table 3. The effect of hydroxy-substituted solvent on the iodine-catalyzed transformations of alcohols **1** under HCRC



Entry	Alcohol			Reaction conditions[a]	Conversion [%][b]	Product distribution[c]		
	Ar	**R¹**	**1**			**2**	**3**	**6/7**
1	Ph	Ph	**b**	CH_2Cl_2 / 67 h	10	100		
2				MeOH / 67 h	0			
3				HCOOH / 23 h	89			100
4				H_2O / 67 h	14	90	10	
5	*p*-An	Ph	**i**	CH_2Cl_2 / 60 min	97	100		
6				MeOH / 20 h	100		5	95
7				HCOOH / 30 min	100	87		13[d]
8				H_2O / 230 min	100	88	12	
9	*p*-An	H	**h**	CH_2Cl_2 / 15 min	92	100		
10				MeOH / 180 min	95	5		95
11				HCOOH / 30 min	98	8		92
12				H_2O / 15 min	96	100		

[a] 1 mmol of **1**, 3 mmol of solvent and 0.03 mmol of I_2 stirred at 25 °C. [b] Conversion and product distribution determined by ^{1}H NMR spectroscopy. [c] Dimerization *vs*. Dehydration *vs*. Substitution. [d] A ratio **2**/**7** without I_2 was 23/77.

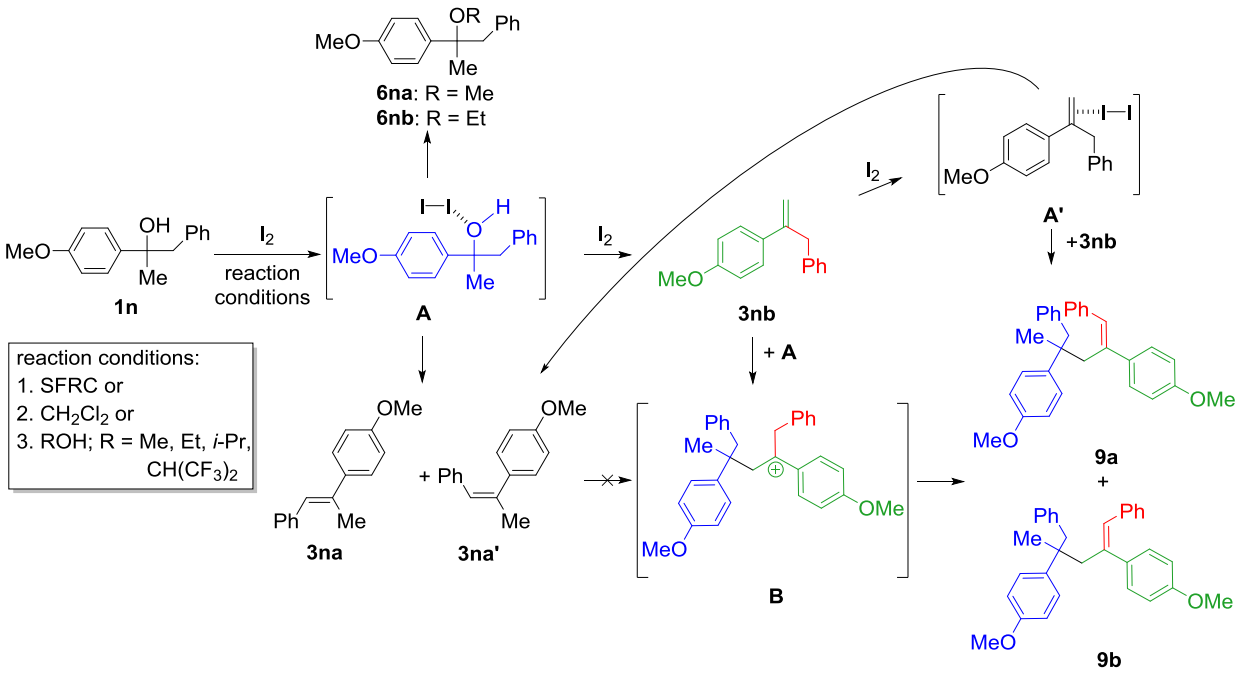
Table 4. The effect of the reaction conditions on the iodine-catalyzed transformation of 4-methoxybenzyl alcohol



Entry	Reaction conditions[a]	Conversion [%][b]	Dimerization / Ipso / Substitution[c] 2m / 8 / 6ma
1	SFRC / 150 min	54	82 / 18
2	HCRC-CH_2Cl_2 / 150 min	37	86 / 14
3	HCRC-MeOH / 190 h	91	10 / 90

[a] SFRC: 1 mmol of **1m** and 0.03 mmol of I_2, HCRC: 1 mmol of **1m**, 3 mmol of solvent and 0.03 mmol of I_2 stirred at 25 °C. [b] Conversion and product distribution determined by ^{1}H NMR spectroscopy. [c] Dimerization *vs*. *Ipso* substitution *vs*. Substitution.

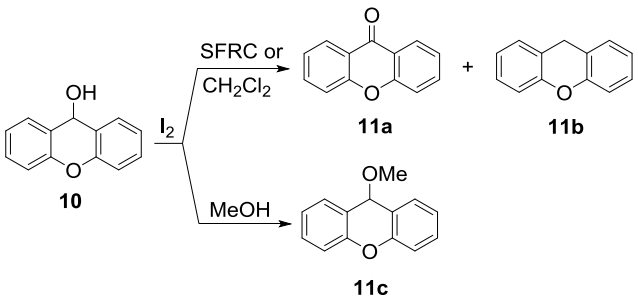
Table 5. The effect of the reaction conditions on the iodine-catalyzed transformations of **1n**



Entry	Reaction conditions[a]	Conversion [%][b]	Product distribution				
			3na'+3na[c]	3nb	9a	9b	6[d]
1	SFRC	100	57		23	20	
2	CH_2Cl_2-3 mmol	100	58		21	21	
3	CH_2Cl_2-30 mmol	98	70	12	8	10	
4	CH_2Cl_2-300 mmol	0					
5	MeOH-3 mmol	78	30	15			55
6	MeOH-30 mmol	68					100
7	MeOH-300 mmol	0					
8	EtOH-3 mmol	61	44	23			33
9	$(CH_3)_2CHOH$-3 mmol	77	67	33			
10	$(CF_3)_2CHOH$-3 mmol	100	72		14	14	

[a] SFRC; 1 mmol of **1n** and 0.03 mmol of I_2, HCRC; 1 mmol of **1n**, 3, 30 or 300 mmol of solvent and 0.03 mmol of I_2 stirred at 25 °C for 30 min. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Data refer to the sum of **3na** and **3na'**, with (*E*)/(*Z*) = 95/5 (entries 1, 5, 8–10) and (*E*)/(*Z*) = 90/10 in entries 2 and 3. [d] Methoxy ether **6na** in the case of MeOH and ethoxy ether **6nb** in the case of EtOH were formed.

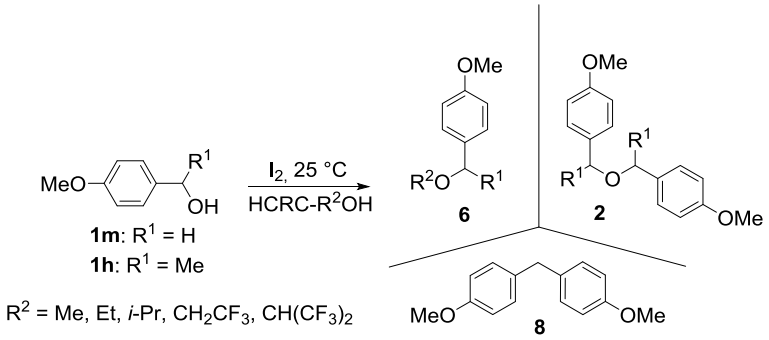
Table 6. The effect of the reaction conditions on iodine-catalyzed transformation of **10**



Entry	Reaction conditions	Conversion (%)[c]	Distibution of products **11a** / **11b** / **11c**
1	SFRC[a] / 15 min	100	50 / 50
2	CH_2Cl_2[b] / 5 min	100	50 / 50
3	MeOH[b] / 5 min	100	100

[a] 1 mmol of **10**, 0.03 mmol of I_2, T = 25 °C. [b] 1 mmol of **10**, 3 mmol of solvent, 0.03 mmol I_2, T = 25 °C. [c] Conversion and product distribution determined by ^{1}H NMR spectroscopy.

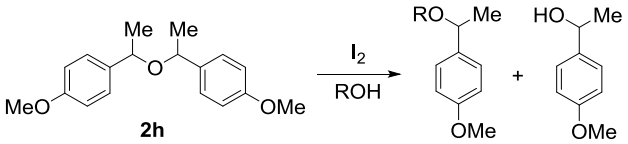
Table 7. The effect of the HCRC on the transformation of **1m** and **1h**



Entry	1	R^2OH	Reaction time[a]	Conversion (%)[b]	Dimerization / Substitution / Ipso				
					2	/	**6**	/	**8**
1	**1m**	MeOH	190 h	91	10	/	90		
2	**1m**	EtOH	360 h	80	16	/	80	/	4
3	**1m**	*i*-PrOH	360 h	67	29	/	64	/	7
4	**1m**	CF_3CH_2OH	1 h	40	77		/		23
5	**1m**	$(CF_3)_2CHOH$	1 h	30	65		/		35
6	**1h**	MeOH	15 min	43	14	/	86		
7	**1h**	MeOH	3 h	95	5	/	95		
8	**1h**	EtOH	15 min	49	61	/	39		
9	**1h**	EtOH	25 h	98	12	/	88		
10	**1h**	*i*-PrOH	15 min	37	80	/	20		
11	**1h**	*i*-PrOH	25 h	98	25	/	75		
12	**1h**	CF_3CH_2OH	15 min	83	20	/	80		
13	**1h**	CF_3CH_2OH	2.5 h	96	8	/	92		
14	**1h**	$(CF_3)_2CHOH$	15 min	60	100				

[a]1 mmol of **1**, 3 mmol of R^2OH, 0.03 mmol of I_2, T = 25 °C. [b]Conversion and product distribution determined by ^1H NMR spectroscopy.

Table 8. The effect of the hydroxy-substituted solvent on the conversion of **2h** under HCRC

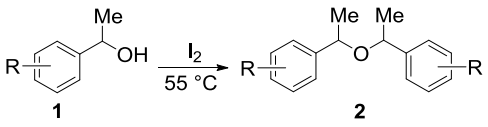


2h **6** **1h**

R = Me, Et, *i*-Pr, CH_2CF_3, Ac

Entry	ROH	Reaction time[a]	Conversion (%)	6 / 1h
1	MeOH	3 h	75	97 / 3
2	EtOH	15 h	74	97 / 3
3	*i*-PrOH	15 h	52	96 / 4
4	CF_3CH_2OH	1.5 h	91	95 / 5
5	CH_3COOH	6 h	79	88[c] / 12

[a] Reaction conditions: 1 mmol of **2h**, 3 mmol ROH, 0.03 mmol of I_2, T = 25 °C, R. t. (reaction time). [b] Conversion and product distribution determined by ^{1}H NMR spectroscopy. [c] The product is 1-(4-methoxyphenyl)ethyl acetate **6he**.



1 2

Entry	R	1	σ+	log k_{rel}
1	4-F	**1o**	−0.07	0.30
2	3-Me	**1p**	−0.07	0.24
3	H	**1a**	0	0
4	3-OMe	**1q**	0.05	−0.10
5	4-Cl	**1r**	0.11	−0.24
6	4-Br	**1s**	0.15	−0.37

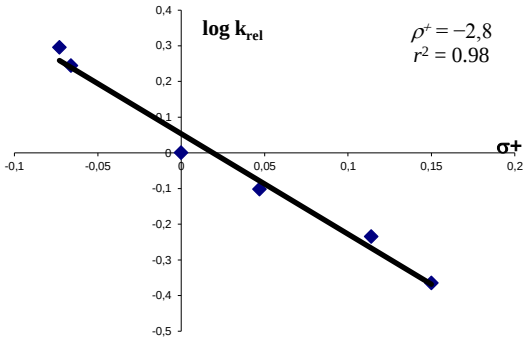
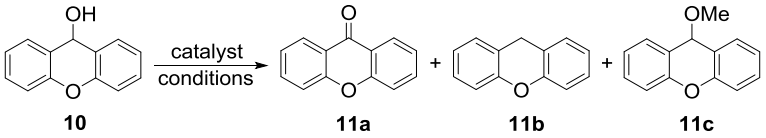


Figure 1. Hammett correlation analysis on I_2-catalyzed dimerization of **1**.

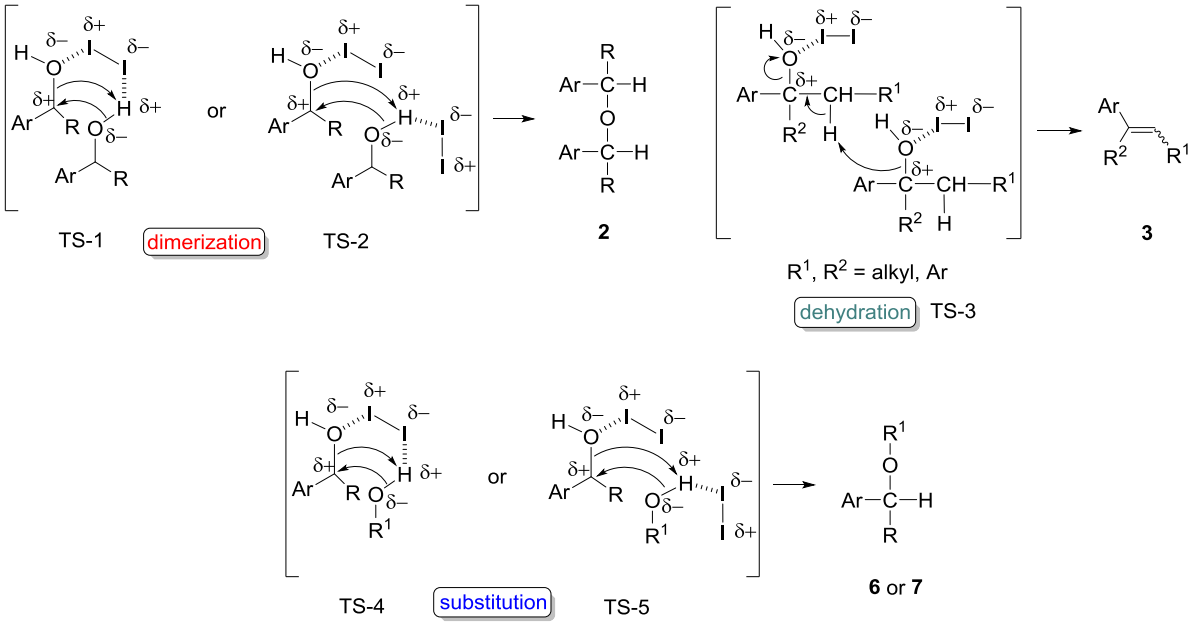
Table 9. Comparison of activity of different catalysts on the transformation of **10**[a]



10 **11a** **11b** **11c**

Entry	Catalyst	Reaction time, rt	Conversion (%)[b]	11a	11b	11c
1	3% I_2/SFRC[c]	15 min	100	50	50	
2	3% I_2/MeOH	5 min	100			100
3	PMA/SFRC[d]	15 min	29[e]	7	7	
4	PMA/MeOH[f]	5 min	100	8	8	84
5	3% HI (57%)[g]	15 min	100	50	50	
6	3% HI (57%)/MeOH[h]	5 min	100	10	10	80
7	3% I_2/3% H_2O/MeOH[i]	5 min	100			100
8	3% I_2/3% KI/SFRC[j]	15 min	46[k]	20	20	
9	3% I_2/3% KI/MeOH[l]	5 min	100			100
10	3% I_2/3% Bu_4NI/SFRC[m]	15 min	40[n]	2	2	
11	3% I_2/3% Bu_4NI/MeOH[o]	5 min	95			100

[a] Reaction conditions: **10** (1 mmol, 198 mg) and various catalysts, R. t. (reaction time), rt. [b] Conversion and product distribution determined by ^1H NMR spectroscopy. [c] Entries 1 and 2 from Table 6. [d] **10** (1 mmol, 198 mg) and phosphomolybdic acid hydrate (PMA, $H_3[P(Mo_3O_{10})_4] \cdot xH_2O$), 60 mg. [e] 71% of unreacted **10** and 15% of a new, unidentified product presumably a ROR type dimer of **10**. [f] **10** (1 mmol, 198 mg), methanol (3 mmol, 96 mg) and PMA (60 mg). [g] **10** (1 mmol, 198 mg) and HI (57 % aqueous solution, 0.03 mmol, 6.7 mg). [h] **10** (1 mmol, 198 mg), methanol (3 mmol, 96 mg) and HI (57 % aqueous solution, 0.03 mmol, 6.7 mg). [i] **10** (1 mmol, 198 mg), H_2O (0.03 mmol, 0.6 mg), methanol (3 mmol, 96 mg) and I_2 (0.03 mmol, 7.6 mg). [j] KI (0.03 mmol, 5 mg) and I_2 (0.03 mmol, 7.6 mg) were stirred for 20 minutes, **10** (1 mmol, 198 mg) was added. [k] 54% of unreacted **10** and 6% of a new product, presumably a ROR type dimer of **10**. [l] KI (0.03 mmol, 5 mg), I_2 (0.03 mmol, 7.6 mg) were stirred for 20 minutes, **10** (1 mmol, 198 mg) and methanol (3 mmol, 96 mg) were added. [m] I_2 (0.03 mmol, 7.6 mg) and Bu_4NI (0.03 mmol, 11.1 mg) were stirred for 20 minutes, **10** (1 mmol, 198 mg) was added. [n] 60% of unreacted **10** and 36% of a new product, presumably a ROR type dimer of **10**. [o] I_2 (0.03 mmol, 7.6 mg), Bu_4NI (0.03 mmol, 11.1 mg) were stirred for 20 minutes, **10** (1 mmol, 198 mg) and methanol (3 mmol, 96 mg) were added.



Scheme 2. A suggested role of iodine in transformation of alcohols under SFRC and HCRC.