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Iodine-catalyzed transformation of molecules containing oxygen functional groups

Marjan Jereb [a,*], Dejan Vražič [b], Marko Zupan [a]

[a] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 1001 Ljubljana, Slovenia
[b] "Jožef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia

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Abbreviations: APSG, aminopropyl silica gel; Bn, benzyl; Boc, *tert*-butyloxycarbonyl; Bz, benzoyl; CBz, benzyloxycarbonyl; DCE, 1,2-dichloroethane; DCM, dichloromethane; DHP, 3,4-dihydro-2*H*-pyran; DMAP, 4-dimethylaminopyridine; DMSO, dimethyl sulfoxide; DS, degree of substitution; EDG, electron-donating group; EWG, electron-withdrawing group; HCRC, highly concentrated reaction conditions; HMDS, hexamethyldisilazane; IC, iodine-catalyzed; ICT, iodine-catalyzed transformation; IMT, iodine-mediated transformation; IPA, isopropenyl acetate; MOM, methoxymethyl; Ms, methylsulfonyl; MW, microwave; NPhth, *N*-phthaloyl; PEG, polyethylene glycol; Pg, protecting group; Piv, pivaloyl; PMB, *p*-methoxybenzyl; PMHS, polymethylhydrosiloxane; PVP, polyvinylpyrrolidone; *t*, reaction time; rt, room temperature; SDS, sodium dodecylsulfate; SFRC, solvent-free reaction conditions; TBDMS, *tert*-butyldimethylsilyl; TBHP, *tert*-butyl hydroperoxide; TEMPO, 2,2,6,6-tetramethylpiperidine 1-oxyl; THF, tetrahydrofuran; THP, tetrahydropyranyl; TMS, trimethylsilyl; TPP, triphenylphosphine; Ts, *p*-toluenesulfonyl; US, ultrasound; VA, vinyl acetate.

* Corresponding author. Tel.: +386 1 241 92 48; fax: +386 241 92 20; e-mail address: marjan.jereb@fkkt.uni-lj.si (M. Jereb).

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1. Introduction

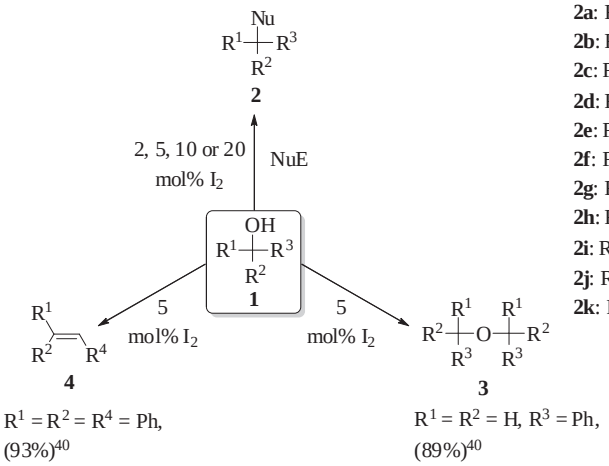
Iodine has been attracting much attention since its discovery in 1811. It is the weakest oxidizer among the halogens and a poor electrophile that often needs the assistance of a strong acid or oxidizer. It is soluble in numerous organic solvents and only slightly soluble in water. The solubility in water may be substantially increased in the presence of dissolved iodides, due to the formation of triiodide ions. One of the remarkable features of iodine is the formation of associates with iodides or triiodides, yielding polyiodides.[1] Polyiodides exhibit a fascinating structural chemistry and have been applied in different fields. In addition to polyiodides, iodine is also capable of complexing oxygen functional groups. This can be concluded from different experiments, as well as from the transformation in which the correct succession of addition of the reactants was crucial to obtain the product.[2] Additional substantiation of this type of complexation was the regioselectivity of the iodination of phenol with iodine/aqueous H_2O_2, yielding a mixture of 2-iodophenol and 2,6-diiodophenol.[3] Iodine has several advantages over the vast majority of the other Lewis-acid catalysts, especially the metallic catalysts. Its catalytic potential is intriguingly broad; it is a water-tolerant, relatively cheap and environmentally friendly catalyst. Another distinctive feature of iodine is its high catalytic activity in dilute solutions, under highly concentrated reaction conditions (HCRC) as well as under solvent-free reaction conditions (SFRC). The latter reaction conditions are particularly important in terms of green chemistry; they contribute to waste- and health-hazard minimization and cost efficiency. Iodine was established as a good mediator and reagent in organic synthesis.[4] For a long time iodine has been recognised as a good catalyst and reagent in carbohydrate chemistry.[5,6] Some examples of iodides in combination with oxidizers were additionally proved to be efficient; the system appeared to function as an iodine precatalyst. Different aspects of iodine chemistry have been reviewed; four reviews in Chinese[7–10] on iodine as a catalyst[11] and the use of iodine in protection/deprotection[12] chemistry have been published recently. However, these papers only partly covered the topic; the most recent 3 years are almost unreviewed. Iodocyclization reactions,[13,14] polyvalent iodine chemistry,[15] iodine as reagent for aromatization,[16] electrophilic iodination with iodine and iodides[17] and oxidative halogenation with 'green' oxidants[18] have also been covered recently. In this report, we present an overview of the iodine-catalyzed transformation of oxygen-containing molecules.

2. Transformation of molecules containing sp^3 hybridized oxygen atoms bound to carbon

2.1. Alcohols

Benzyl,[19–24] allyl[22,25–31] and propargyl[22,32,33] alcohols **1** reacted with various nucleophiles in the presence of 2–20 mol % of I_2 and formed different types of products **2a**–**2k** (Scheme 1, Table 1). Aliphatic tertiary alcohols were treated with NaSCN and oxalic acid in nitromethane to yield the corresponding thiocyanates, which underwent isomerization to isothiocyanates if 50 mol % of I_2 was present.[34,35] Iodine in combination with silphos, $[PCl_{3-n}(SiO_2)_n]$, a heterogenous catalyst promoted thiocyanation of benzylic alcohols.[36]

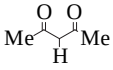
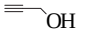
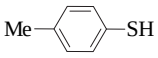
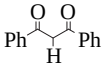
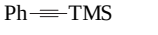
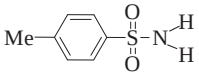
The property of iodine to catalyze the elimination of water from hydroxy compounds has been known for almost a century,[37–39] while primary and secondary benzylic alcohols furnished ethers, such as **3** (R^1=R^2=H; R^3=Ph) at elevated temperatures under SFRC.[40] A combination of I_2/Ph_3P was an efficient dehydrating agent;[41] I_2/Ph_3BiBr_2 was applied as a dehydrating agent of secondary and tertiary alcohols.[42] Tertiary alcohols underwent elimination of water in the absence of nucleophile, furnishing the corresponding alkenes, such as **4** (R^1=R^2=R^4=H) in high yield (Scheme 1).[40] 1,3-Diaryl propargyl alcohols were transformed into 3-aryl-1*H*-indenes by means of 2 equiv of triethylsilane and 10 mol % of iodine in 1,2-dichloroethane at 80 °C.[43]



2a: R^1 = Ph, R^2 = H, R^3 = CHCHPh, Nu = allyl,[25]
2b: R^1 = Ph, R^2 = H, R^3 = Me, Nu = $CH(COMe)_2$,[19]
2c: R^1 = 4-$OMeC_6H_4$, R^2 = H, R^3 = Me, Nu = OCH_2CCH,[20]
2d: R^1 = Me, R^2 = H, R^3 = CHCHPh, Nu = 4-MeC_6H_4S,[26]
2e: R^1 = Ph, R^2 = H, R^3 = CCPh, Nu = 4-OHC_6H_4,[32]
2f: R^1 = 4-MeC_6H_4, R^2 = H, R^3 = CHCH(4-MeC_6H_4), Nu = $CH(COPh)_2$,[27,28]
2g: R^1 = Ph, R^2 = H, R^3 = Nu = CCPh,[33]
2h: R^1 = 4-MeC_6H_4, R^2 = H, R^3 = CHCHPh, Nu = NHTs,[29,30]
2i: R^1 = R^2 = Ph , R^3 = H, Nu = NHCOPh[22]
2j: R^1 = Ph, R^2 = R^3 = H, Nu = 4-$OMeC_6H_4$,[21]
2k: R^1 = Ph, R^2 = H, R^3 = Me, Nu = NHCOMe[23]

Scheme 1. IC substitution, dimerization or elimination of alcohols.

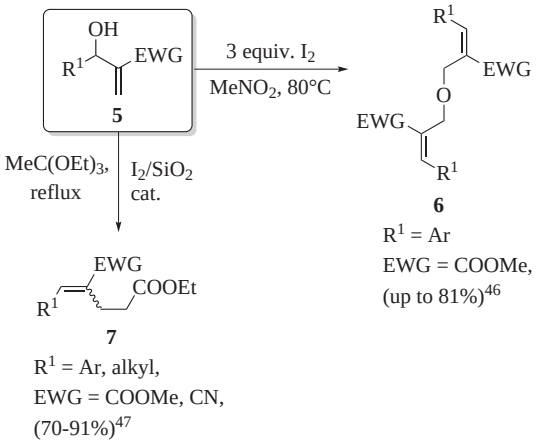
Table 1
IC nucleophilic substitutions of alcohols **1**

NuE	Reaction conditions[a] I_2 (mol %)/*T*/solvent/*t*	Product	Yield (%)	Ref.
	10/rt/CH_2Cl_2/0.25 h	**2a**	94	25
	10/80 °C/$MeNO_2$/1 h	**2b**	99	19
	5/0 °C/MeCN/0.25 h	**2c**	92	20
	10/rt/1,4-Dioxane/1.5 h	**2d**	92	26
Phenol	5/-10 °C/MeCN/0.5 h	**2e**	90	32
	5/rt/CH_2Cl_2/1.5 h	**2f**	90	27,28
	10/0 °C/CH_2Cl_2/3 h	**2g**	96	33
	5/rt/CH_2Cl_2/3 h[a]	**2h**	85	29,30
$PhCONH_2$	2/Reflux/MeCN/2 h	**2i**	98	22
Anisole	10/60 °C/SFRC/4 h[b]	**2j**	88	21
$MeCN/H_2O$	20/110 °C/PhMe/4 h[c]	**2k**	85	23

[a] Reaction was carried out in the presence of $CaSO_4$.
[b] Reaction was carried out in the presence of molecular sieves.
[c] Water (2 equiv) was added.

Iodine catalyzed reaction of tertiary alcohols with primary or secondary alcohols afforded the corresponding *tert*-butyl ethers at 100 °C in a hydrogen atmosphere at 80 bar in 10 min.[44] **IC** transformation of α-vinylbenzyl alcohols in MeCN in the presence of alcohols furnished cinnamyl ethers. Primary alcohols reacted more smoothly than secondary and tertiary; 1-phenylallyl cation was proposed as the key intermediate.[45]

The Baylis–Hillman–adducts **5** were converted with 3 equiv of iodine into symmetrical bisallylic ethers **6** with exclusive (*E*) geometry (Scheme 2), while the transformation proceeded best in $MeNO_2$ at 80 °C, but the amount of iodine is of vital importance.[46] Iodine adsorbed on silica gel efficiently catalyzed the Johnson–Claisen rearrangement of Baylis–Hillman allylic alcohols **5** when



Scheme 2. ICT of Baylis-Hillman adducts.

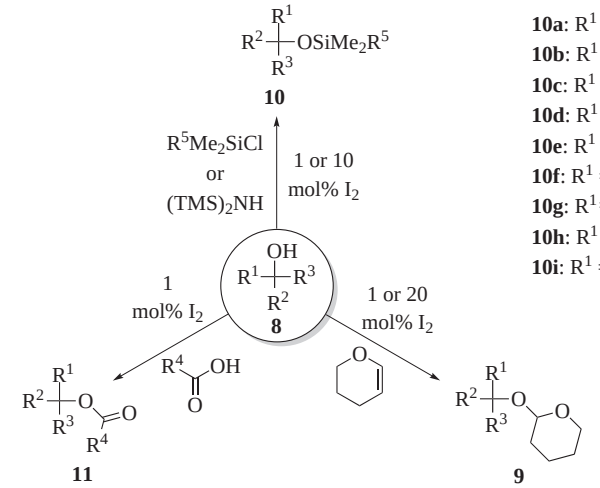
treated with triethyl orthoacetate. Ethyl alk-4-enoate derivatives **7** were obtained with good (*E*)- and (*Z*)-selectivity, which depended on the structure of the starting alcohol (Scheme 2),[47] but dimerization of benzylic alcohols bearing EDGs was also observed in **IC** esterification with carboxylic acids.[48]

Highly selective **IC** etherification of the pharmaceutically interesting molecule, morroniside, furnished its 7-*O*-alkyl ethers in reasonable yields.[49] 2-Tetrahydropyranyl ethers are important in protection chemistry, and the reactions of alcohols **8** with DHP were studied (Scheme 3). Primary, secondary, tertiary aliphatic, benzylic alcohols and phenols were successfully converted into the corresponding tetrahydropyranyl ethers **9**,[50–53] while Table 2 shows the effect of reaction variables on the yield of the tetrahydropyranylation of benzyl alcohol. Besides molecular iodine, in situ-generated I_2 from NaI and $Fe(NO_3)_3 \cdot 9H_2O$ was also demonstrated to be an efficient catalyst.[52] Polyhydroxy alcohols were

Table 2
IC tetrahydropyranylation of benzyl alcohol under various reaction conditions

Alcohol/DHP	Reaction conditions I_2 (mol %)/*T*/solvent/*t*	Yield (%)	Ref.
1/1.3	20/—/SFRC/7 min[a]	91	50
1/1	1/rt/CH_2Cl_2/30 min	90	51
1/1.4	—/rt/CH_2Cl_2/5 min[b]	96	52

[a] MW irradiation of reaction mixture, temperature was not defined.
[b] Mixture of 1.4 mol % of $Fe(NO_3)_3 \cdot 9H_2O$ and 2.6 mol % of NaI was used instead of I_2.



10a: R^1 = heptyl, $R^2 = R^3$ = H, R^5 = Me,[58]
10b: R^1 = Ph, $R^2 = R^3$ = H, R^5 = Me,[58]
10c: R^1 = Ph, $R^2 = R^3$ = H, R^5 = *t*-Bu,[57]
10d: $R^1 + R^2 = (CH_2)_5$, R^3 = H, R^5 = Me,[57]
10e: $R^1 + R^2 = (CH_2)_5$, R^3 = H, R^5 = *t*-Bu,[57]
10f: $R^1 = CH_2(CH_2)_{13}Me$, $R^2 = R^3$ = H, R^5 = Me,[57]
10g: $R^1 = CH_2(CH_2)_{13}Me$, $R^2 = R^3$ = H, R^5 = *t*-Bu,[57]
10h: $R^1 = R^2 = R^3 = R^5$ = Me,[57]
10i: $R^1 = R^2 = R^3$ = Me, R^5 = *t*-Bu[57]

Scheme 3. IC etherification and esterification of alcohols.

selectively tetrahydropyranylated, e.g., 1,2-ethanediol could be converted into the monoprotected ether in 78% yield.[53]

Amounts of iodine for the promotion of silylation protection of alcohols **8** ranged from 1 mol %[54,55] and up to twofold excess.[56] Excellent yields were obtained with aliphatic and benzylic alcohols, as presented in Table 3; phenol underwent silylation giving the ether in 95% yield.[57] The utilized silylating reagents were HMDS,[54,55,58] TMSCl and TBDMSCl,[57] although other reagents in combination with *N*-methylimidazole also proved efficient.[56] In situ-generated I_2 from $Fe(NO_3)_3\cdot 9H_2O$/NaI,[59] from KI/H_5IO_6[60] and HIO_3/KI[61] was also an effective catalyst for silylation.

Table 3
IC conversion of alcohols into silyl ethers **10**

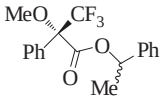
Alcohol	Reagent	**10**	Yield (%)	Ref.
1-Octanol	HMDS[a]	**10a**	92	58
Benzyl alcohol	HMDS[a]	**10b**	98	58
	TMSCl[b]	**10b**	95	57
	TBDMSCl[c]	**10c**	94	57
Cyclohexanol	TMSCl[b]	**10d**	93	57
	TBDMSCl[c]	**10e**	95	57
1-Hexadecanol	TMSCl[b]	**10f**	96	57
	TBDMSCl[c]	**10g**	94	57
tert-Butanol	TMSCl[b]	**10h**	90	57
	TBDMSCl[c]	**10i**	92	57

[a] Alcohol (10 mmol), HMDS (8 mmol) and I_2 (0.1 mmol) stirred in DCM less than 5 min at rt.
[b] Alcohol (2 mmol), TMSCl (2.6 mmol) and I_2 (0.2 mmol) irradiated in 1,2-dichloroethane (DCE) with MW for 2 min.
[c] Alcohol (2 mmol), TBDMSCl (3 mmol) and I_2 (0.2 mmol) irradiated in DCE with MW for 2 min.

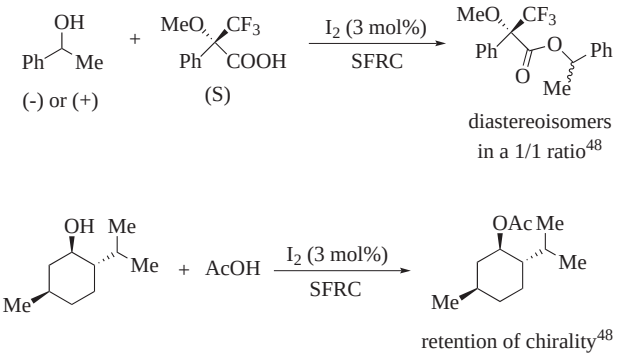
Iodine exhibited high catalytic activity for the preparation of esters **11** from primary, secondary and tertiary aliphatic alcohols; transformations were carried out with different acylating sources: carboxylic acids,[48,62] acetic anhydride,[63–66] vinyl acetate (VA)[67] and isopropenyl acetate (IPA)[68] were used most frequently.

A large excess of alcohol, carboxylic acid and 1 mol % of I_2 was refluxed from four to 20 h,[62] while Table 4 summarizes the role of reaction conditions and acyl source on the esterification of 1-phenylethanol. Saturated, unsaturated, hydroxy and dicarboxylic acids were esterified with primary, secondary and tertiary aliphatic alcohols in high yield, while benzoic acid did not react, but the esterification conditions exhibited good tolerance of water.[62] It was established that acetylation of aliphatic alcohols with acetic acid proceeded with the retention of stereochemistry, while the esterification of benzylic alcohols furnished esters with lost stereochemical integrity (Scheme 4).[48] Iodine is also able to promote transesterifications.[62,69–71]

Table 4
IC esterifications of 1-phenylethanol

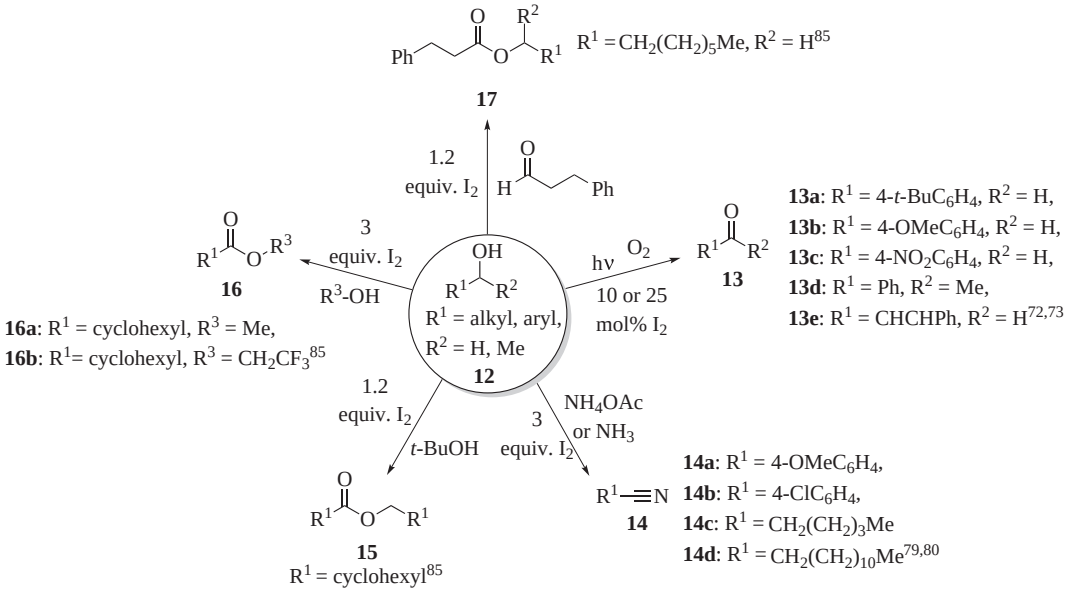
Acyl source	Reaction conditions I_2 (mol %)/*T*/solvent/*t*	Product	Yield (%)	Ref.
Ac_2O	10/rt/SFRC/3 min		97	64
Vinyl acetate	10/rt/SFRC/5 h		93	67
Mosher's acid	3/rt/SFRC/166 h		86[a]	48

[a] Conversion given. A mixture of diastereoisomeric esters in 1/1 ratio.



Scheme 4. Dual behaviour of alcohols in **IC** esterification.

IC oxidative transformations of alcohols are presented in Scheme 5 and in Tables 5–7. Aerobic photocatalytic oxidation of benzylic and allylic alcohols **12** into the corresponding aldehydes and ketones **13**



Scheme 5. **IMT** of alcohols.

Table 5
IC aerobic photooxidation of alcohols

Entry	Alcohol	*t*/conditions[a]	**13**	Yield (%)
1	4-*t*-Bu$C_6H_4CH_2OH$	3.5 h/A	**13a**	80
2		24 h/B		87
3	4-OMe$C_6H_4CH_2OH$	3 h/A	**13b**	92
4		24 h/B		87
5	4-$NO_2C_6H_4CH_2OH$	8 h/A	**13c**	55
6		24 h/B		81
7	$C_6H_5CHOHCH_3$	3 h/A	**13d**	90
8	$C_6H_5CHCHCH_2OH$	6 h/A	**13e**	85
9		24 h/B		56

[a] A: 1 mmol of alcohol, 0.25 mmol of I_2, 25 mL of MeCN equipped with O_2-baloon, strirred at rt and irradiated with high pressure 400 W mercury lamp.[72]

B: 0.3 mmol of alcohol, 0.03 mmol of I_2 and 5 mL of EtOAc equipped with O_2-baloon, stirred at rt and irradiated with four 22 W fluorescent lamps.[73]

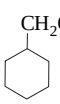
Table 6
IMT of benzylic and aliphatic alcohols into nitriles

Entry	Alcohol	*t*/conditions[a]	**14**	Yield (%)
1	4-OMe$C_6H_4CH_2OH$	2 h/A	**14a**	92
2		2 h/B		99
3	4-Cl$C_6H_4CH_2OH$	2 h/A	**14b**	93
4		2 h/B		95
5	$CH_3(CH_2)_4CH_2OH$	10 h/A	**14c**	65
6	$CH_3(CH_2)_{11}CH_2OH$	8 h/B	**14d**	91

[a] A: 1 mmol of alcohol, aq NH_4OAc (3 mL, 30 mmol) and 3 mmol of I_2 stirred at 100 °C.[79]

B: 1 mmol of alcohol, aq NH_3 (3 mL, 45 mmol) and 3 mmol of I_2 stirred at 60 °C.[80]

Table 7
IMT of primary alcohols[85]

Entry	Alcohol	Reaction conditions[a] I_2 (equiv)/*T*/solvent/*t*	Product	Yield (%)
1	*n*-Octanol	1.2/rt/*t*-BuOH/22 h[b]	**17**	91
2		1.2/rt/*t*-BuOH/27 h	**15**	93
3		3/70 °C/MeOH/23 h	**16a**	70
4		3/50 °C/CF_3CH_2OH/15 h[c]	**16b**	91

[a] Conducted in inert atmosphere in the presence of K_2CO_3: 3 equiv in entries 1, 3 and 4 and 5 equiv in entry 2, 0.5 mL of solvent.

[b] $Ph(CH_2)_2CHO$ was added to the reaction mixture. Equivalents of added I_2 are relative to aldehyde.

[c] Solvent (5 mL).

was carried out and, interestingly, no over-oxidation to acids was observed, while the double bond in allylic alcohols remained intact. Primary benzylic alcohols containing EDGs were more reactive than alcohols bearing EWGs (Table 5, entries 3 and 5),[72] but increasing amounts of iodine had a negative effect on the yield.[73]

When (diacetoxyiodo)benzene was used as an oxidant, benzylic, allylic and aliphatic alcohols were efficiently oxidized to carboxylic acids and ketones in MeCN, while esters were formed in the presence of MeOH.[74]

IC oxidation of benzylic alcohols to the related carbonyl derivatives under MW irradiation in triglyme took place at 130 °C. A cyclic transition state between iodine and alcohol was proposed; the formation of HI and its re-oxidation to iodine in the presence of oxygen was suggested as being the driving force of the catalytic cycle.[75]

Oxidation of primary and secondary benzylic alcohols to the carbonyl derivatives in ionic liquids was studied with an excess of I_2 and Li_2CO_3.[76] Iodine was utilized as a chemoselective terminal oxidant of TEMPO in oxidation reactions of alcohols.[77] A three-component system, consisting of I_2, KI and K_2CO_3, was established as effective for the oxidation of aryl and alkyl alcohols into aldehydes and ketones. The optimal reaction medium was water; no over-oxidation of primary alcohols to acids took place, and secondary alcohols did not undergo α-iodination.[78]

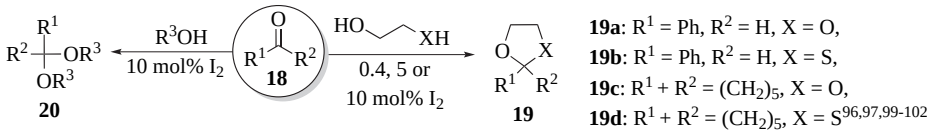
Benzylic and aliphatic alcohols were converted into nitriles **14** in the presence of a twofold excess of iodine in aqueous NH_4OAc and, as evident from Table 6, aliphatic alcohols are less reactive than their benzylic counterparts (entries 1 and 5).[79] The same transformation could also be accomplished in aqueous NH_3 using an excess[80] of I_2 or with TBHP and a catalytic amount of I_2.[81] Later, the method was further developed and applied, e.g., under MW irradiation, a direct conversion of primary alcohols and aldehydes into triazines and tetrazoles took place, although the amount of aqueous NH_3 was increased as well as iodine (4 equiv).[82] Primary amides were obtained from 1-arylethanols or methyl ketones when subjected to 3 or 4 equiv of I_2 in aqueous NH_3. The proposed reaction pathway involves the oxidation of alcohol to the methyl ketone and a subsequent Lieben iodoform reaction.[83] Similarly, benzylic alcohols were transformed into amides upon treatment with excess of I_2 and H_2O_2 in aqueous NH_3.[84]

The combination of I_2/K_2CO_3 in different solvents was effective in oxidative conversions of various aliphatic and aromatic alcohols (Scheme 5 and Table 7) to esters **15**–**17**, ketones and aldehydes;[85] the latter can be further transformed into benzimidazole and imidazoline derivatives.[86] The yield of oxidative esterification of alcohols with aldehydes depended on electronic effects and decreased with growing steric hindrance. If the primary aliphatic or benzylic alcohols were stirred in *t*-BuOH without aldehyde at rt in the presence of I_2/K_2CO_3, the condensed esters **15** were obtained (Table 7, entry 2) in high yield (70–93%). In MeOH or in 2,2,2-trifluoroethanol, the corresponding methyl **16a** (entry 3) or 2,2,2-trifluoroethyl esters **16b** (entry 4) were obtained in excellent yield.[85] Iodine in combination with lead tetraacetate was utilized in the synthesis of epoxycycloalkane derivatives.[87]

Iodine also acted as a catalyst in combination with other reagents and/or co-catalysts. Lanthanum metal, TMSCl and catalytic amounts of CuI and I_2 were efficient in a deoxygenative coupling of alcohols producing alkane derivatives as the main products. Concomitantly, a simple reduction of alcohols furnished alkanes as side products.[88,89] H_3PO_2 and a stoichiometric amount of iodine served as an efficient system for the reduction of benzylic alcohols to the corresponding alkanes.[90,91] The $I_2/NaHCO_3$ system promoted intramolecular cyclization of *N*-propargyl-β-hydroxymethyl enamides to 1,4-oxazepines.[92] I_2/(diacetoxy)iodobenzene promoted β-fragmentation of steroidal alcohols to γ-lactones;[93] in addition, the unexpected formation of orthoacetate ester was noted.[94] Iodine was found to be an excellent promoter of cyclization of *ortho*-hydroxyalkylaryl substituted sulfonamides into five-membered benzosultams.[95]

IC acetalization of carbonyl compounds **18** with 2-mercaptoethanol,[96] primary aliphatic alcohols and diols furnished thiolane derivatives **19** and ketals/acetals **20** (Scheme 6).[97–99] Several procedures were developed for acetalization with 1,2-ethanediol, as presented in Table 8. Aldehydes reacted in MeOH in the presence of 10 mol % of iodine much faster than ketones (Table 8, entries 1 and 2).[98] MW irradiation of a mixture of aldehyde or cyclic ketone with 1,2-ethanediol in THF with I_2 gave products with yields of up to 98%, while the acyclic ketones remained unchanged.[100] Similar results were published previously, with the additional finding that the reaction tolerated up to 25% of water.[97] Re-usable reaction systems have already received some attention; but there is still a lack of more intensive focus on the sustainable systems.

Ionic liquids were tested as media for **IC** acetalization of aliphatic and aromatic carbonyl compounds, although aliphatic derivatives (in general) gave higher yields. The I_2/ionic liquid (IL 400) system could be re-used sixfold (entries 7 and 8);[101] iodine adsorbed on polyaniline could not be re-used (entries 3 and 4),[102] while iodine-doped chitosan could be re-used fivefold (entries 11 and 12).[103]



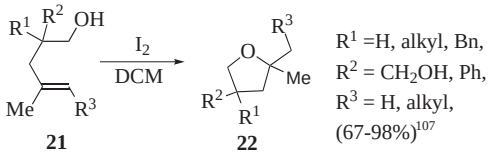
Scheme 6. IC acetalization of carbonyl compounds.

Table 8
Effect of reaction conditions on **IC** acetalization of benzaldehyde and cyclohexanone

Entry	Alcohol	Carbonyl compound	Reaction conditions I_2 (mol %)/*T*/solvent	Reaction Time	Acetal	Yield (%)	Ref.
1	MeOH	PhCHO	10/—/MeOH[a]	1 h	**20a**	98	98
2	MeOH	Cyclohexanone		8 h	**20b**	90	98
3	Glycol	PhCHO	0.4/Reflux/cyclohexane[b]	2 h	**19a**	77	102
4	Glycol	Cyclohexanone		2 h	**19c**	86	102
5	Glycol	PhCHO	5/—/Glycol [a]	16 h	**19a**	70	99
6	Glycol	Cyclohexanone		16 h	**19c**	90	99
7	Glycol	PhCHO	5/rt/Glycol+IL 400	Several min	**19a**	83	101
8	Glycol	Cyclohexanone		Several min	**19b**	96	101
9	Glycol	PhCHO	10/—/THF[a,c]	7 min	**19a**	85	97
10	Glycol	Cyclohexanone		4 min	**19c**	92	97
11	Glycol	PhCHO	0.2/Reflux/cyclohexane[d]	2 h	**19a**	86	103
12	Glycol	Cyclohexanone		2 h	**19c**	92	103
13	HS OH	PhCHO	5/—/SFRC[a,c]	3 min	**19b**	83	96
14	HS OH	Cyclohexanone		3 min	**19d**	95	96

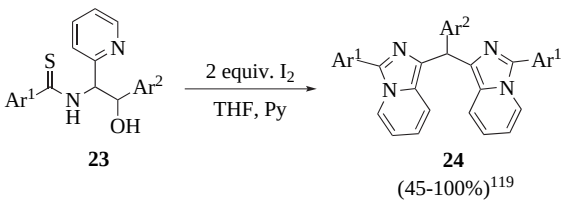
[a] Temperature not given.
[b] Iodine adsorbed on polyaniline.
[c] MW irradiation of reaction mixture.
[d] Iodine adsorbed on chitosan.

These are the main topics that have been researched the most in the **ICT** of alcohols. Reactions like the selective O-alkylation of alcohols,[104] direct oxidative conversion of alcohols into 2-imidazolines and 2-oxazolines,[105] Prins cyclization,[106] cyclization of alkenols **21** to THF derivatives **22** (Scheme 7),[107] cyclization of 1,3-diols,[108,109] ring opening of epoxides and episulfides,[110] synthesis of 1,2,4,5-tetraarylimidazoles,[111] synthesis of pyranobenzothiopyrans and furanobenzothiopyrans,[112] glycosylation[113,114] and other[115–118] reactions also involve the use of iodine as a catalyst.



Scheme 7. IC cyclization to tetrahydrofurans.

One-pot **IC** cyclization of *N*-thioacyl-1-(2-pyridyl)-1,2-amino-alcohols **23** and subsequent condensation to the bis(1-imidazo[1,5-*a*]pyridyl)arylmethanes **24** proceeded efficiently in THF at rt (Scheme 8).[119]



Scheme 8. One-pot synthesis of symmetrical *N*-heterocycles.

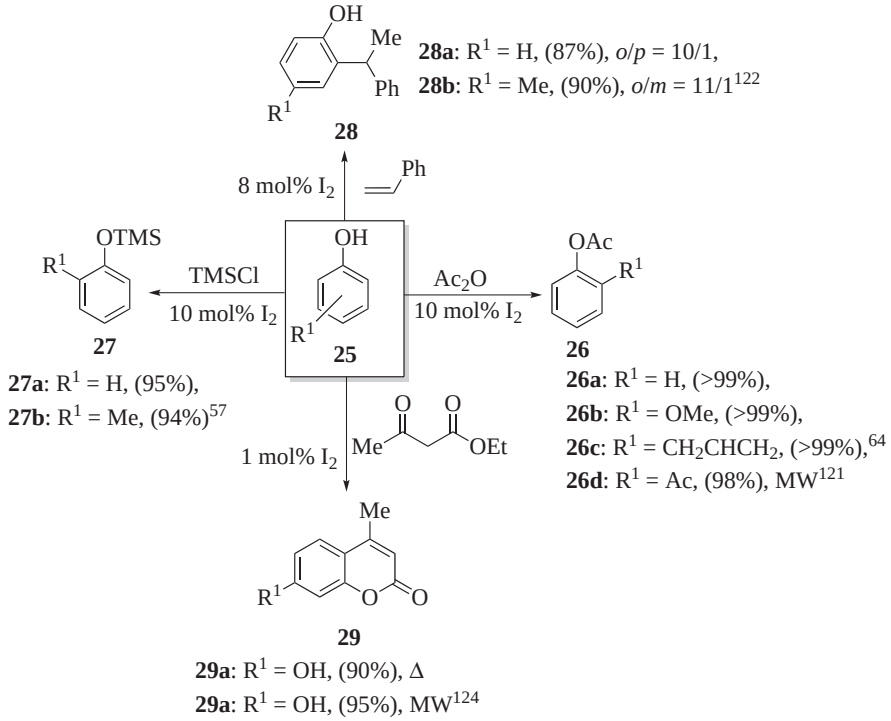
The majority of articles do not mention any experimental investigation of the mechanism of iodine-mediated transformation, although one report (based on spectroscopic measurements) suggested the formation of charge-transfer complexes between alcohol and I_2 in iodine-catalyzed alkoxy-alkoxy exchange reactions of alkylalkoxysilanes.[120]

2.1.1. Phenols. Phenols **25** were transformed into acetates **26** in high yield using Ac_2O or IPA[68] in solution[63] and under SFRC.[64] Sterically hindered and deactivated phenols were acetylated with the aid of MW irradiation (Scheme 9),[121] while the yields being remarkably higher under MW than in a classical heated reaction. Phenols were derivatized into TBDMS and TMS ethers **27** by means of I_2 as catalyst. Products were obtained in high yield in both cases; although TBDMSCl exhibited lower reactivity than TMSCl.[57] Silylation of phenols with HMDS was also feasible with in situ-generated I_2 from $Fe(NO_3)_3 \cdot 9H_2O$/NaI,[59] from KI/H_5IO_6[60] and HIO_3/KI.[61] **IC** tetrahydropyranylation of phenol or naphthol afforded the corresponding ethers after 2–3 h in 82 and 80% yield, respectively.[51]

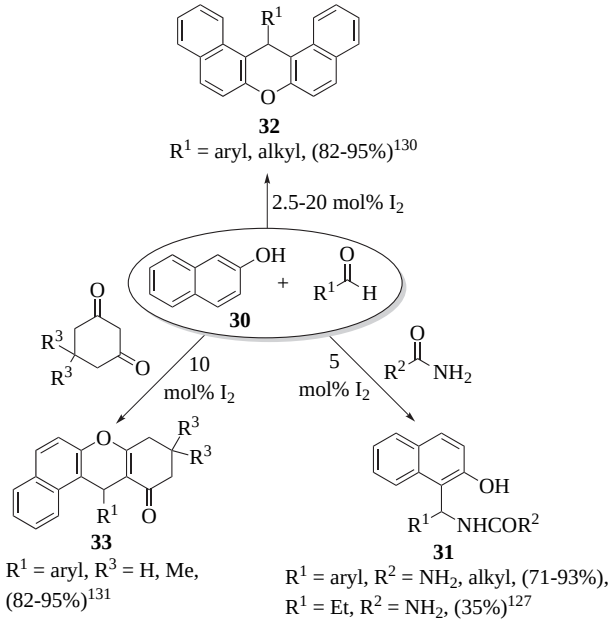
Iodine was found to be capable of catalyzing electrophilic aromatic substitution of phenols.[20] Styrenes reacted highly regioselectively with phenols, yielding 1,1-diarylalkanes **28** in good yields (Scheme 9).[122]

IC Pechmann condensation of phenols and β-ketoesters to coumarins **29** was studied in toluene;[123] shortly afterwards, another group discovered that the reaction could be carried out under SFRC at 85 °C, or, with improved yields, under MW at 110 °C (Scheme 9, **29a**).[124]

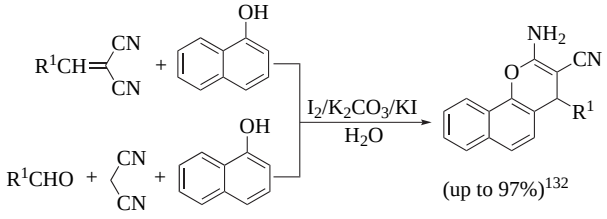
Several other functionalizations of phenols were also accomplished (Schemes 10 and 11). A combination of naphthol **30**, benzaldehyde and acetonitrile afforded acetamidophenols **31**, while aromatic nitriles failed to react (Scheme 10).[125] Similarly, in the presence of urea or amide, **30** and benzaldehyde furnished



Scheme 9. ICT of phenols.



Scheme 10. IC three-component reactions of phenols.



Scheme 11. One-pot synthesis of chromene derivatives.

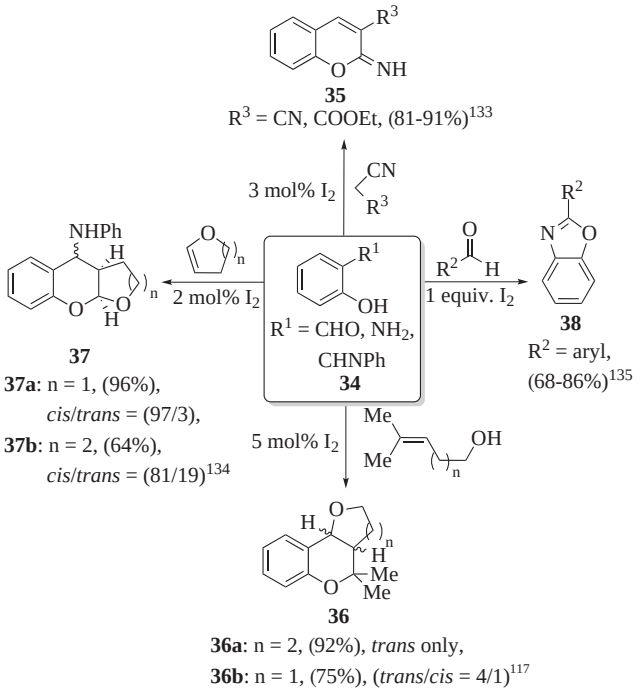
amidoalkyl naphthols **31**, the highest yields being obtained in chlorinated solvents.[126] Aromatic aldehydes underwent facile conversion, whereas the aliphatic ones afforded products in low yield.[127] Biologically active 14-aryl(alkyl)-14*H*-dibenzo[*a*,*j*]xanthenes **32** were obtained from 2-naphthol and aromatic and aliphatic aldehydes, the amount of iodine ranging from 2.5 to 20 mol %.[128–130] Reactions performed under MW irradiation and under SFRC required much shorter reaction times than reactions in solution;[128,129] interestingly, increasing the amount of iodine seemed to have a negative effect on the reaction time.[129,130]

Instead of urea, cyclic 1,3-dicarbonyl compounds were used in the condensation reaction, giving the corresponding 12-aryl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one derivatives **33**[131] (Scheme 10).

Condensation of arylidenemalononitriles and 1-naphthol could be efficiently catalyzed by the I_2/K_2CO_3 system, giving 2-amino-2-chromenes[132] (Scheme 11).

A two-component **ICT** of *ortho*-substituted phenols **34** led to the formation of diverse heterocyclic systems (Scheme 12). I_2/K_2CO_3-promoted condensation of **34** with activated methylene compounds followed by cyclization led to the benzopyran framework **35** (Scheme 12). Interestingly, the transformation proceeded more effectively in water than in EtOH.[133] The hetero-Diels–Alder reaction of **34** with 5-methylhex-4-en-1-ol and trimethyl orthoformate in the presence of 5 mol % I_2 in CH_2Cl_2 at rt led to the stereoselective formation of *trans*-fused pyrano[3,2-*c*]benzopyran **36a**. In contrast, fusion of *o*-hydroxybenzaldehyde with 4-methylpent-3-en-1-ol led to the formation of a stereoisomeric mixture of tetrahydrofuro[3,2-*c*]benzopyran **36b**.[117]

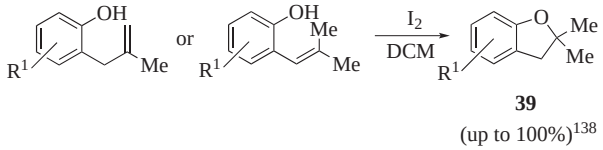
Only 2 mol % of I_2 were found to be necessary to catalyze the synthesis of *cis*-fused pyranobenzopyrans and furanobenzopyrans **37** from *o*-hydroxybenzaldimines and 2,3-dihydrofuran or 3,4-dihydro-2*H*-pyran (Scheme 12). The diastereoselectivity of the reaction was markedly affected by the solvent.[134] The **IC** formation of 2-arylbenzoxazoles **38** from 2-aminophenol and aromatic aldehydes has been reported. Oxidation of the intermediary Schiff base to the product required a stoichiometric amount of I_2.[135] A



Scheme 12. **IC** cyclizations of *ortho*-substituted phenols.

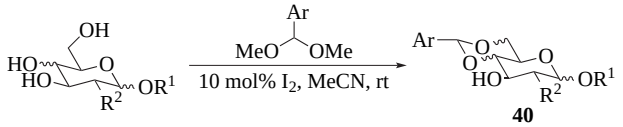
subsequent publication revealed that the same reaction could be carried out with 0.5 equiv of iodine and without solvent; MW irradiation substantially accelerated the reaction.[136] Schiff bases generated from salicylaldehyde and aryl amines underwent iodine-promoted cyclization into the corresponding 1,2-benzisoxazoles.[137]

IC cyclization of *o*-alkenyl-substituted phenols in DCM yielded 2,3-dihydrobenzofurans **39** as the sole products (Scheme 13).[138] A nitro-substituted starting material failed to give any desired product, while the reaction worked well with bonded EDGs.



Scheme 13. **IC** formation of dihydrobenzofurans.

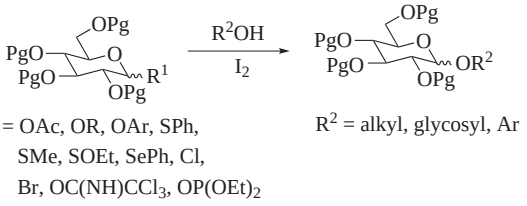
2.1.2. Carbohydrates. Iodine has been known as an efficient catalyst for the transformation of carbohydrates for a long period of time.[139] **ICT** of carbohydrates embraces the protection of hydroxy functional groups as acetals, esters or ethers. Acetal protection has been accomplished with iodine in acetone at 28 °C, affording the corresponding *O*-isopropylidinated carbohydrates;[140] furthermore, the synthesis of benzylidene acetals **40** was achieved with benzaldehyde dimethylacetal in the presence of 10 mol % of I_2 (Scheme 14). The reaction was completed within 1.5 h; the yield was very good and unaffected by scale up.[141] **IC** regioselective reductive ring opening of 4,6-*O*-benzylidene acetals of carbohydrates in the presence of triethylsilane afforded 6-*O*-benzyl derivatized



Scheme 14. Benzylidene protection of carbohydrates.

products. Ester, NPhth, ether, thioether and selenoether functionalities remained intact.[142]

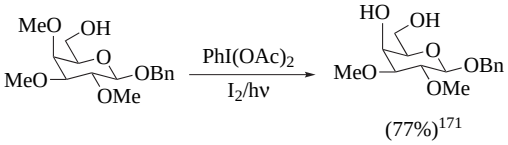
Protected carbohydrates[143,144] could be further transformed in the presence of I_2; several nucleophilic substitutions were performed and the anomeric position exhibited the highest reactivity (Scheme 15).[145–153] In the case of aliphatic alcohols[154] and hydroxy-substituted amino acids[155] as nucleophiles, **IC** glycosylation took place alone; in the case of alkyl and aryl mercaptans[156] as nucleophiles, the I_2/Fe couple was an effective catalyst. **IM** N- and C-glycosylation of hemiketals with $TMSN_3$ and TMSCN, respectively, furnished substituted cyano and azido ketosides in good to excellent yields.[157]



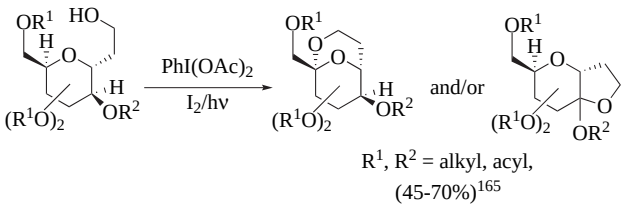
Scheme 15. **IC** nucleophilic substitution reactions.

Per-*O*-acetylated mono- and di-saccharides underwent **ICT** to 1,2-*trans*-bonded 1-thioglycosides.[158] Interestingly, a two-way protection of carbohydrates took place under SFRC with VA or IPA. Besides acetylation, acetalization or ketalization were the competitive reaction pathways; selectivity was found to be temperature dependent. Acetonide acetate was obtained at lower temperatures, while peracetate was formed at higher temperatures.[159] IC one-pot, consecutive acetalation–esterification yielded the orthogonally protected glycosides in good to excellent yields.[160] The I_2/hexamethyldisilane system in MeCN was found to be effective in the anomerization of peracetylated 1,2-*trans*-bonded alkyl and aryl glycosides. In situ-formed TMSI was proposed as the key player in this isomerization reaction.[161]

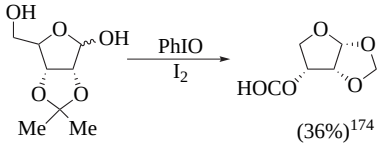
Iodine and (diacetoxy)iodobenzene and the I_2/PhIO system promoted several radical fragmentation and cyclization reactions of carbohydrate derivatives (Schemes 16–18).[162–174] Terminal diols of cyclic and acyclic saccharides were converted by means of two



Scheme 16. $PhI(OAc)_2/I_2$-promoted selective demethylation.



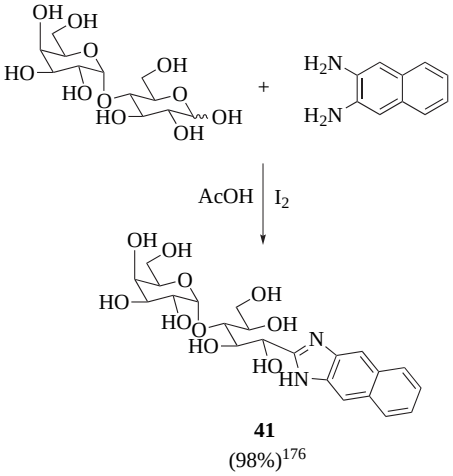
Scheme 17. Regioselective hydrogen-atom abstraction reaction.



Scheme 18. Tandem β-fragmentation-cyclization reaction.

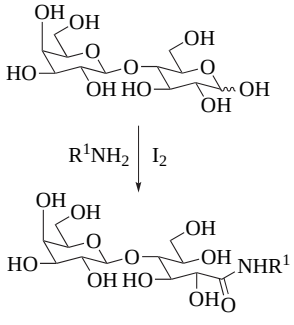
mol equiv of I_2/PPh_3/imidazole at low temperatures (−8 to+15 °C) into the corresponding epoxides.

In contrast, the transformation of diols in refluxing toluene in the presence of four mol equiv of I_2/PPh_3/imidazole resulted in the formation of the corresponding terminal alkenes.[175] Iodine successfully promoted the direct oxidative condensation of aldoses with *o*-arylenediamines to the corresponding aldo-benzimidazole and aldo-naphthimidazole analogues, e.g., **41**; the latter are strongly fluorescent materials (Scheme 19). Reactions were performed in acetic acid solution; the glycosidic bond, and the hydroxy, carboxy and amido moieties remained intact, with no racemization occurring.[176,177] Additionally, iodine promoted the amidation of aldoses and decarboxylative amidation of α-keto acids; the method worked with many different amines, and was compatible with the glycosidic bond and the hydroxy groups; moreover, the stereochemical integrity was preserved (Scheme 20).[178]



41
(98%)[176]

Scheme 19. IC oxidative condensation of aldoses and diamines.



(up to 98%)[178]

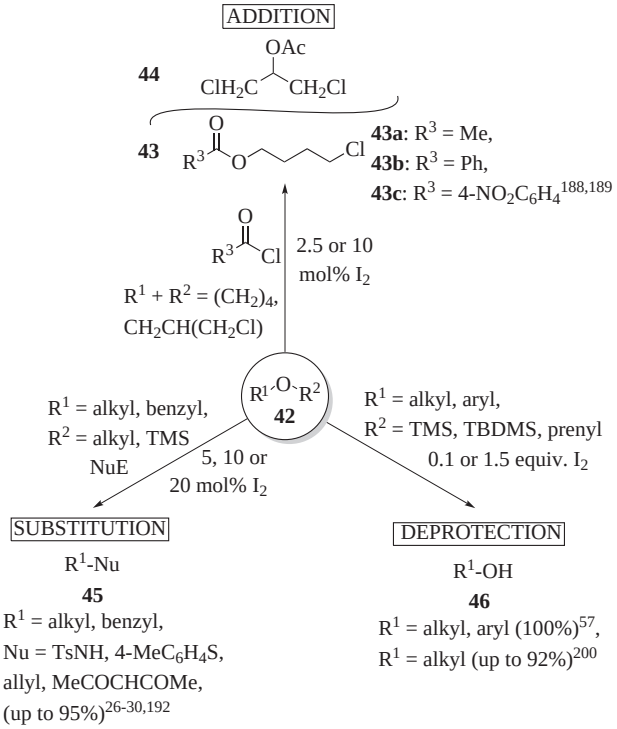
Scheme 20. IC oxidative amidation of aldoses.

IC per-O-acylation of cyclodextrins with carboxylic anhydrides under SFRC gave products in good to high yields.[179] Esterification of cellulose,[180–182] wheat-straw hemicelluloses,[183] starch[180,184] and dextran[185] with Ac_2O was reported. In order to esterify cellulose, up to 15 mol % of I_2 was used;[182] the reaction was conducted at 100 °C under SFRC[180] or with a reduced level of solvent (Ac_2O) at rt or at 100 °C[181] or between 80 and 130 °C with the aid of MW irradiation.[182]

Wheat-straw hemicelluloses were acetylated in a 1-butyl-3-methylimidazolium chloride ionic liquid; 83% of hemicellulose hydroxy groups could be acetylated under the optimized reaction conditions (100 °C, 30 min, 15% I_2), using the Ac_2O/I_2 system. Acetylation of starch at 100 °C proceeded within 10 min,[180] while under MW irradiation it took only 2 min.[184] The degree of substitution on starch proportionally increased with the added quantity of I_2 or Ac_2O and reached a maximum value of 3. Iodine effectively catalyzed the succinoylation of cellulose in a mixture of ionic liquid and DMSO at elevated temperature.[186] **IC** methyl glycosidation of pentoses and 6-deoxyhexoses took place in methanol at reflux in 6–8 h.[187]

2.2. Ethers

Ethers **42** were cleaved with iodine in the presence of aromatic or aliphatic acyl chlorides, and the corresponding esters **43** and **44** (Scheme 21) were formed in high yield (Table 9) at ambient temperature; 10 mol % of I_2 and a ninefold excess of ether relative to acyl chloride were used.[188] Later, it was found that much less iodine was necessary and that the reaction time could be significantly reduced. Ring opening of THF with benzoyl chloride was also very efficient with iodine, below 1 mol %;[189] in the absence of benzoyl chloride, I_2 can cause polymerization of THF.[190] Treatment of alkyl-aryl ethers and other electron-rich aromatic molecules with $POCl_3$ and DMF, followed by reaction with 2 equiv of I_2 in ammonia water afforded the corresponding nitriles in yields of up to 99%.[191]



Scheme 21. ICT of ethers.

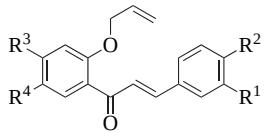
Table 9
IC cleavage of cyclic ethers

Ether	Acyl chloride	Ester	*t* (min)	Yield (%)	Ref.
	MeCOCl[a]	**43a**	120	91	188
	PhCOCl[a]	**43b**	120	93	188
	MeCOCl[b]	**43a**	3	96	189
	PhCOCl[b]	**43b**	5	94	189
	4-$NO_2C_6H_4COCl$[b]	**43c**	10	89	189
	MeCOCl[a]	**44**	240	85	188

[a] Reaction conditions: 6.9 mmol of ether, 0.69 mmol of acyl chloride and 0.069 mmol of I_2 stirred at rt under nitrogen atmosphere.

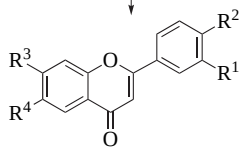
[b] Reaction conditions: 10 mL of ether, 10 mmol of acyl chloride and 0.25 mmol of I_2 stirred at 25 °C under nitrogen atmosphere.

Chalcols and their ether derivatives **42** underwent nucleophilic substitutions in the presence of 5–10 mol % of I_2, producing identical products **45** in excellent yield (Table 10);[26,27,29] furthermore, chalcols could smoothly dimerize to ethers **42**. Aliphatic secondary, tertiary and benzylic TMS ethers underwent direct coupling with allylsilanes to the corresponding terminal alkenes in the presence of 20 mol % of I_2 and 5 mol % of $InCl_3$ (Table 10).[192] Hydrolysis of ethers was carried out with various I_2/solvent combinations, which exhibited different deprotection selectivity, depending on the amount of iodine, solvent and temperature. Silyl ethers were easily and quantitatively transformed into alcohols **46** by treatment with 10 mol % of iodine in MeOH under MW irradiation.[57] Alkyl TBDMS ethers were selectively cleaved over aryl TBDMS ethers with 1 wt % solution of I_2 in MeOH in excellent yield.[193] Selective deprotection with a 1 w/v% solution of I_2 in MeOH at reflux was also feasible, since OPMB together with the isopropylidene group were selectively removed, while OBn and OBz moieties remained intact.[194] Silphos and iodine catalyzed thiocyanation of silyl and THP ethers with NH_4SCN in refluxing MeCN.[36]



47

I_2 | DMSO

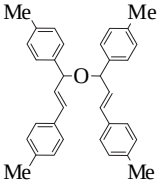
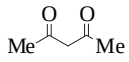
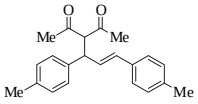
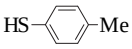
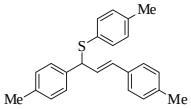
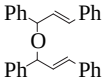
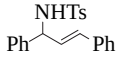
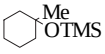
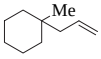


48

R^1 = H, OMe, NO_2, R^2 = H, OMe,
R^3 = H, OBn, R^4 = H, Me, Cl,
(85-97%)[199]

Scheme 22. IC synthesis of flavones **48**.

Table 10
IC nucleophilic substitution of ethers

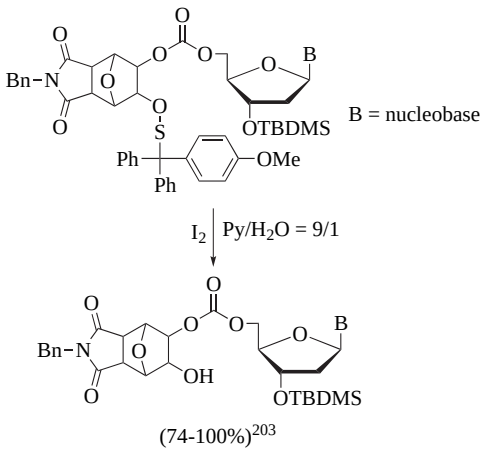
Ether	NuE	Reaction conditions I_2 (mol %)/*T*/solvent/*t*	Product	Yield (%)	Ref.
		10/rt/CH_2Cl_2/16 h		95	27,28
		10/rt/1,4-Dioxane/1.5 h		85	26
	$TsNH_2$	5/rt/CH_2Cl_2/16 h		95	29,30
		20/rt/CH_2Cl_2/3 h[a]		70	192

[a] $InCl_3$ (5 mol %) was added.

Later, it was established that the 1 w/v% solution of I_2 in MeOH (the only difference was a shorter reaction time) was suitable for the concomitant removal of the OTBDMS and OPMB groups, while OMe, OBn, OBz, OTs, OMs, OAc and the isopropylidene group remained untouched.[195] In contrast, the 20 (w/w%) solution of I_2 in MeOH was found to be a stronger and less selective deprotecting agent, since it brought about the hydrolysis of the *O*-isopropylidene, *O*TBDMS, *N*-(9-phenylfluoren-9-yl) and *N*-benzyloxycarbonyl groups simultaneously, followed by cyclization.[196,197]

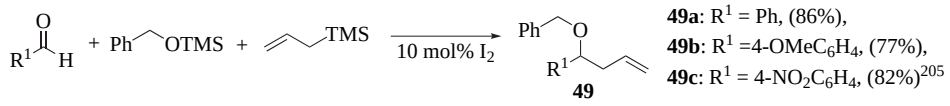
Depending on the concentration of iodine in MeOH, a different degree of selectivity was achieved at different temperatures. At rt, the deprotection of 1-*O*-alkyl-2-*O*-acetyl-3-*O*-trityl glycerol furnished two isomers selectively, 1-*O*-alkyl-2-*O*-acetyl glycerol and 1-*O*-alkyl-3-*O*-acetyl glycerol, but at 60 °C removal of the trityl and acetyl groups took place yielding the 1-alkyl glycerol.[198] Iodine in hot DMSO promoted the removal of *O*-allyl protection of chalcone derivatives **47** followed by cyclization to the flavones **48** (Scheme 22).[199]

Oxidative scission of the prenyl ethers in DCM required 1.5–3 equiv of iodine. Other protecting groups present in the molecule, i.e., acetals, acetates, allylic, benzylic or TBDPS functionalities, stayed unaffected under the mentioned reaction conditions (Scheme 21).[200,201] The I_2/$NaBH_4$ system in dry THF selectively catalyzed deprotection of allylic ethers; Bn, THP, TBDMS, COOMe and acetonide functionalities were compatible with the reacting system.[202] Efficient deprotection of tetrahydropyranyl ethers with I_2/MeOH required reflux conditions[51] or MW irradiation.[50] Iodine promoted selective cleavage of the S–O bond in protected 5-hydroxyl nucleosides;[203,204] the OTBDMS group remained intact (Scheme 23). Removal of tritylthio and 4-methoxytritylthio groups occurred in few minutes with 0.1 M I_2 in pyridine/H_2O solution.



Scheme 23. IC removal of 4-methoxytritylthio group.

Iodine was also capable of catalyzing the three-component reaction of aromatic aldehydes, TMS ethers and allytrimethylsilane, thus forming the homoallyl benzyl ethers **49** in moderate-to-high yields (Scheme 24).[205] Iodine was established as an effective catalyst together with CuI, lanthanum metal and TMSCl in a reductive dimerization of ethers to the corresponding hydrocarbons.[88,89] Iodine efficiently catalyzed the synthesis of *N*-substituted pyrroles from 2,5-dimethoxytetrahydrofuran with both aromatic and aliphatic amines under SFRC using MW activation.[206]



Scheme 24. IC three-component synthesis of homoallyl ethers **49**.

Stereospecific glycosylation of *cis*-1-(*p*-anisyl)-3-hydroxy-4-phenyl-2-azetidinone furnished after hydrolysis both enantiopure α-hydroxy-β-lactams, synthons of Taxol® and related drugs.[113] **IC** glycosylation of the hydroxyethyl-substituted β-lactam gave two separable diastereomeric glycosides, which upon acidic hydrolysis produced two enantiomerically pure β-lactam analogues.[216]

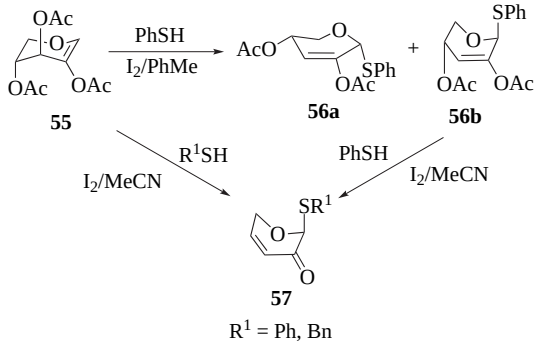
ICT of cyclic or acyclic enol ethers **58** with *N*-arylimines or aromatic aldehydes and amines produced a tetrahydroquinoline framework **59** (Scheme 27).[217–221] The solvents of choice were DCM, MeCN and THF, which proved to be crucial. Mixtures of cis/trans isomers were formed; the latter was predominant in most of the cases. The reaction of anilines bearing EWGs resulted in low yields and longer reaction times. Reportedly, the reaction rate increased with increasing amount of iodine up to 50 mol %.[217] Interestingly, shortly after this study, a paper appeared claiming that the reaction yield deteriorated with increasing amount of iodine (Table 11).[218]

2.2.1. Enol ethers. A Ferrier rearrangement of cyclic enol ethers was catalyzed by iodine (Scheme 25). Alcohols, phenols[207] and thiophenols[208] were glycosylated with 3,4,6-tri-*O*-acetyl-D-glucal **50** (R^1=R^2=R^3=OAc). The reaction was completed within a few hours, with sterically hindered alcohols being less reactive (**51a** and **51c**); the α-anomer was preferred over the β-anomer in all cases.[207,208]

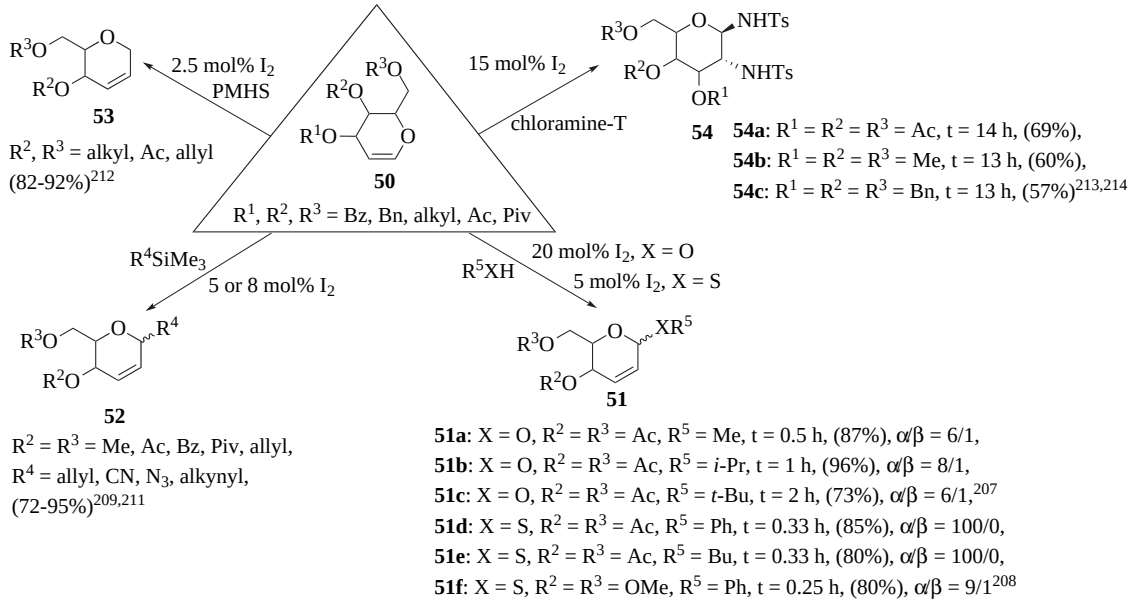
A stereoselective glycosylation of **50** with alkynylsilanes,[209,210] allyltrimethylsilane, TMSCN or $TMSN_3$[211] in DCM furnished glycosyl derivatives **52** at rt with 5–8 mol % of I_2.

A twofold excess of polymethylhydrosiloxane (PMHS) and 2.5 mol % of I_2 smoothly converted glycals into the 3,6-dihydropyran derivatives **53**; Et_3SiH/I_2 also worked well.[212] Glycals **50** were stereoselectively converted into diamino analogues **54** using 2.3 equiv of chloramine-T and 15 mol % of I_2. A single diastereoisomer was formed, having amino functionalities *anti* to each other. Side products originating from the iodine-catalyzed Ferrier rearrangement were not observed. Di-saccharide and tri-saccharide glycals were also diaminated with yields of up to 79%, although higher amounts of chloramine-T and I_2 were necessary.[213,214]

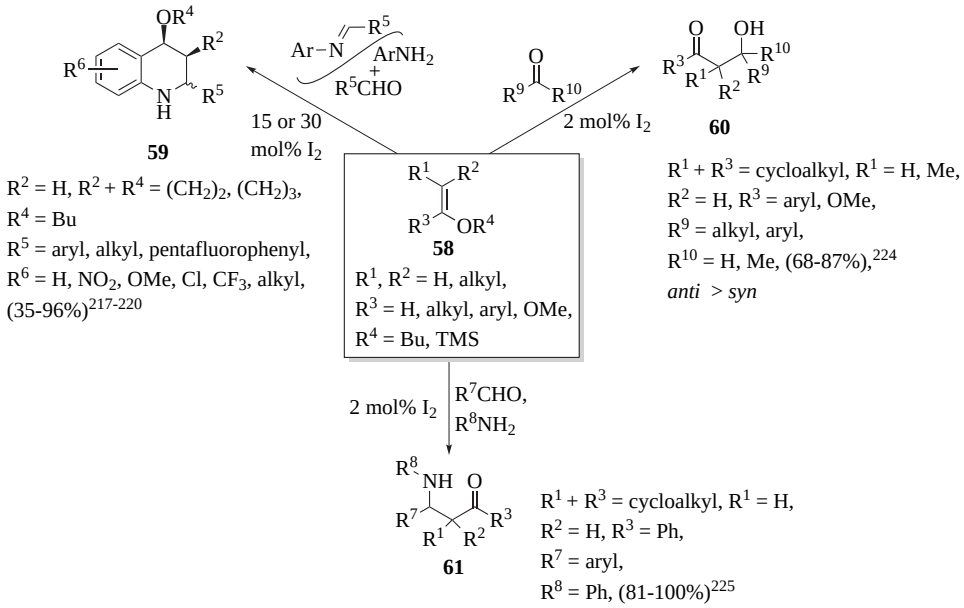
Treatment of 2,3,4-tri-*O*-acetyl-D-xylal **55** with thiophenol in toluene in the presence of iodine afforded a mixture of α/β-anomers of the phenylthio-substituted glycal derivative **56a** and **56b**. Transformation in MeCN selectively produced 2(*S*)-2-phenylthio-2*H*-pyran-3(6*H*)-one **57**, obtained via two allylic rearrangements. Rearrangement to the dihydropyranone proceeded faster in polar than in nonpolar solvents (Scheme 26).[215]



Scheme 26. IC functionalization of xylal **55**.

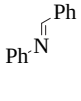
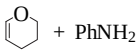


Scheme 25. IC Ferrier rearrangement of glycals.



Scheme 27. **IC** of enol ethers.

Table 11
IC synthesis of tetrahydroquinoline framework **59**

Reactants		*t* (h)	Product ratio cis/trans	Yield (%)	Ref.
		12[a]	32/68	74	218
		12[a]	59/41	54	218
		12[a]	10/90	35	218
	PhCHO	3[b]	23/77	84	217
	3-$NO_2C_6H_4CHO$	4[b]	26/74	79	217
	4-$OMeC_6H_4CHO$	3[b]	9/91	84	217

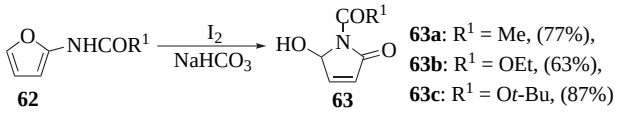
[a] Reaction conditions: 1 mmol of imine, 2 mmol of enol ether, 0.15 mmol of I_2, 5 mL of CH_2Cl_2 stirred at rt.
[b] Reaction conditions: 2 mmol of aldehyde, 2 mmol of aniline, 4 mmol of 2,3-dihydropyran, 10 mL of MeCN and 30 mol % of I_2 stirred at rt.

In contrast, tetrahydroquinolines **59** could be obtained in high yield in the presence of 20 mol % of I_2 from anilines and 2,3-dihydrofuran or 3,4-dihydro-2*H*-pyran. A stereoisomeric product mixture contained *endo* and *exo* isomers; the latter was the predominant in most cases.[222] This reaction found an interesting application in the **IC** synthesis of cryptotackiene scaffold, a linear indolo[2,3-*b*]quinoline alkaloid.[223] Silyl enol ethers have a wide range of applications and have been extensively used in various reactions. The Mukaiyama aldol reaction of silyl enol ethers with aldehydes and ketones was efficiently catalyzed by I_2, hence yielding β-hydroxy carbonyls **60** in moderate-to-good yield.

The *anti* stereoisomer was predominant and aromatic aldehydes reacted faster than aliphatic aldehydes.[224] In addition, iodine catalyzed a three-component transformation of aniline, aldehyde and silyl enol ether into β-amino ketones **61** (Scheme 27).[225] In the case of carboxybenzylamine, the carboxybenzyl-protected β-amino esters could be synthesized.[226]

Iodine catalyzed a stereoselective Michael addition of 2-trimethylsilyloxyfuran to α,β-unsaturated ketones. The yield of γ-butenolides was as high as 93%, with the *syn* stereoisomer as the major product.[227] 2-Trimethylsilyloxyfuran underwent addition to aldehydes in the presence of 10 mol % of I_2 in DCM yielding δ-silyloxy-α,β-unsaturated-γ-lactones at rt, whereas hydroxy derivatives were obtained with improved *syn* stereoselectivity in Et_2O at −78 °C.[228]

Furyl-substituted compounds also participated in **IC** redox reactions. 2-Amidofurans **62** underwent a novel oxidative rearrangement in aqueous $NaHCO_3$ with 3 equiv of I_2, furnishing 5-hydroxy-1*H*-pyrrol-2(5*H*)-ones **63** (Scheme 28).[229]



Scheme 28. **IC** oxidative rearrangement of 2-amidofurans **62**.

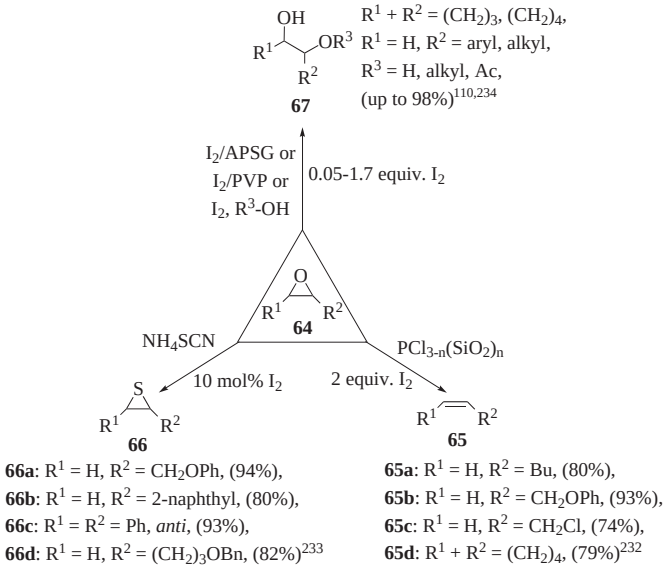
Furthermore, furan and 2-methylfuran were transformed into (*E*,*E*)-sulfono- and phosphono-ω-acyl-functionalized dienes with neopentyl α-diazomethanesulfonate and di-*iso*-propyl α-diazomethanephosphonate, respectively.[230]

Some theoretical ab initio MO calculations of the **IC** Mukaiyama aldol reaction were performed. It was shown that the reaction of trihydrosilyl enol ether with formaldehyde is more likely to proceed in a concerted manner, while the reaction of 1-phenyl-1-(trimethylsilyloxy)ethylene and benzaldehyde was more likely to occur via a stepwise mechanism. The calculations indicated the complexation of iodine and the oxygen atom of the silyl enol ether or aldehyde.[231]

2.2.2. Epoxides. Reaction of epoxides **64** with I_2 and heterogeneous Silphos ($PCl_{3-n}(SiO_2)_n$) in dry DMF resulted in the formation of alkenes **65** (Scheme 29) as exclusive products. The ratio of reactants was found to be of vital importance for the selective transformation; 1 g of Silphos, 2 mmol of I_2 and 1 mmol of epoxide were used. A change in this ratio altered the reaction pathway, furnishing a mixture of products.[232] Iodine was shown to catalyze the transformation of epoxides to thiiranes **66** by using NH_4SCN in MeCN; acid-sensitive protecting groups, e.g., THP or TBDMS, remained unaffected during the process.[233] Furthermore, iodine catalyzed the ring opening of epoxides in the presence of nucleophiles to the corresponding hydroxy derivatives **67** (Table 12).

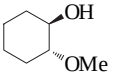
It was established that loading of I_2 on polyvinylpyrrolidone (PVP)[234] or aminopropyl silica gel (APSG)[110] did not contribute to the loss of catalytic activity.

Alcoholysis, hydrolysis and acetolysis of epoxides proceeded under different reaction conditions; the trans isomer was obtained



Scheme 29. ICT of epoxides.

Table 12
IC epoxide opening reactions

Epoxide	I_2 (mol %)	Solvent	T (°C)	t (min)	Product	Yield (%)
	10[a]	MeOH	25	60	$PhCH(OMe)CH_2OH$	98
	20[b]	MeOH	25	90	$PhCH(OMe)CH_2OH$	92
	6[c]	MeOH	25	10	$PhCH(OMe)CH_2OH$	95
	100[a]	*t*-BuOH	85	20	$PhCH(Ot\text{-}Bu)CH_2OH$	60
	80[b]	*t*-BuOH	85	60	$PhCH(Ot\text{-}Bu)CH_2OH$	60
	10[c]	*t*-BuOH	85	75	$PhCH(Ot\text{-}Bu)CH_2OH$	75[d]
	10[a]	MeOH	25	45		98
	20[b]	MeOH	25	330		91
	20[c]	MeOH	25	45		95

[a] Iodine without support.[234]
[b] Iodine supported on polyvinylpyrrolidone.[234]
[c] Iodine supported on aminopropyl silica gel.[110]
[d] 1-Phenyl-1,2-ethanediol (15%) was also formed.

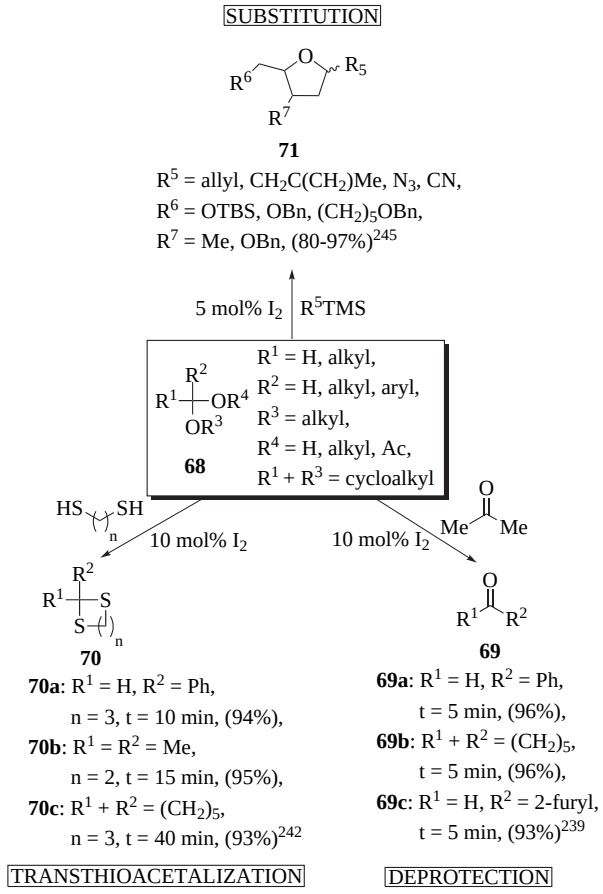
as the sole product. Iodine adsorbed on silica gel is not a stable catalyst because of the slow evaporation of iodine, contrary to the immobilization on APSG. Transformation of terminal epoxides in acetone in the presence of I_2 resulted in the formation of iodohydrins and acetonides, whereas internal epoxides furnished iodohydrins as the exclusive products.[235]

2.3. Acetals and ketals

Since acetals and ketals **68** are actually protected aldehydes and ketones, iodine was successfully employed for deprotection, either with I_2/MeOH[236–238] or I_2/Me_2CO systems (Scheme 30).[239]

Deprotection of dialkyl acetals and ketals with 10 mol % of I_2 in acetone to carbonyls **69** was rapid; moreover, additional double bond, hydroxy, ketoxime, *tert*-butyl and acetate groups remained intact during the reaction as well as an acid-sensitive furyl functionality in **69c**.[239] The terminal isopropylidene group could be chemoselectively cleaved in the presence of an internal isopropylidene group with 10 or 30 mol % of I_2 in MeCN. Deprotection was completed within a few hours; groups like OPMB, OMe, OAc, MOM, OBn, *O*-allyl and *O*-propargyl remained unaffected, while TBS, TBDPS, TMS, THP moieties did not survive.[240]

In situ-formed I_2 from $CuSO_4$/NaI in acetone catalyzed the deprotection of acetals and ketals.[241] Thioacetals **70** were obtained

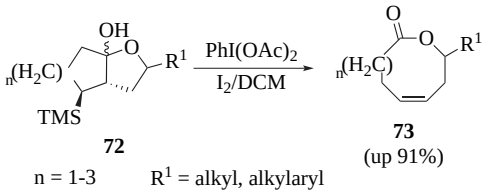


Scheme 30. ICT of acetals and ketals.

via transthioacetalization of acetals and ketals in the presence of 10 mol % of I_2 and dithiols with yields of up to 96%. No side products were formed; I_2/PVP was also found to be effective.[242] Iodine on alumina catalyzed the deprotection of 1,3-oxathiolanes and 1,3-dithiolanes in aqueous solution; the method was attuned with benzyl, allyl and acetyl functionalities.[243] Regeneration of carbonyl molecules from 1,3-dithianes and 1,3-dithiolanes with 30% H_2O_2 in an aqueous micellar system using SDS was effectively catalyzed by iodine. The method exhibited tolerance to OAc, *O*-allyl, OTBDMS, OTBDPS, OCOPh, Bn, amino, hydroxy, NHCbz and NHBoc groups without over-oxidation.[244]

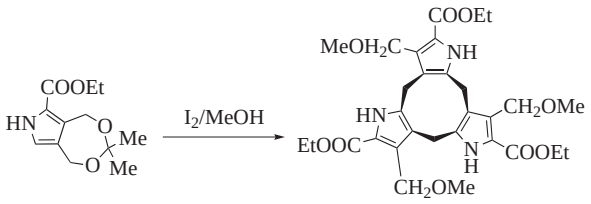
Acetals can act as protecting agents, which was shown in the **IC** reaction of sugars with benzylidene dimethylacetal.[141] Substitution of five-membered lactol ethers with TMS reagents at −78 °C in DCM proceeded with high diastereoselectivity in the presence of 5 mol % I_2, giving allyl, azido and nitrile derivatives **71**.[245] Iodine in equimolar amounts concomitantly with $PhI(OAc)_2$ promoted regiospecific oxidative ring expansion of γ-lactols **72** to unsaturated homoallylic lactones **73** (Scheme 31).[246]

Unusual **IC** cyclotrimerization of a pyrrole analogue in methanol yielded the cyclononatripyrrole scaffold **74**, a potential



Scheme 31. I_2/$PhI(OAc)_2$-promoted oxidative ring expansion.

macromolecular building block for supramolecular chemistry (Scheme 32).[247]



74

Scheme 32. IC cyclotrimerization of pyrrole derivative.

Cyclic steroidal peroxyhemiacetals were stereospecifically transformed into 1,2-dioxolane derivatives by means of I_2/(diacetoxyiodo)benzene in DCM.[248] Iodine promoted the ionic Diels–Alder reactions of protected and unprotected α,β-unsaturated acetals with 1,3-dienes to the corresponding cycloadducts. DCM was the optimal reaction medium, the reaction exhibiting good *endo* selectivity.[249]

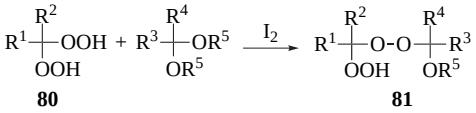
2.3.1. Orthoesters. Iodine was found to be a suitable catalyst for the transformation of orthoesters **75**. Substituted indoles and triethyl orthoformate in MeCN and 15 mol % of I_2 yielded the triindolylmethanes **76** (Scheme 33). No by-products were detected; EWGs decreased the reactivity of indoles.[250] This reaction was successfully performed under SFRC with 5 mol % I_2, the electronic effects were the same and the yields were also high.[251]

2-Substituted benzimidazoles **77** and 2-substituted phenanthrimidazoles **78** were prepared in an **IC** condensation. The former were obtained from 1,2-phenylenediamines and orthoesters: EWGs on the phenyl ring exerted a negative effect on the reactivity and the yield.[252] Condensation of 9,10-phenanthraquinone, orthoester and NH_4OAc in EtOH produced **78**.[253] Iodine-catalyzed condensation of orthoesters, anthranilic acid and amine yielded 3,4-dihydroquinazolin-4-ones **79** under SFRC,[254,255] while EWGs on the ring of the aniline decreased the reactivity.[254] Similarly, **79** could be obtained in **ICT** of triethyl orthoester, aryl amines and isatoic anhydride in ethanol or water.[256]

IC O-alkylation of alcohols[104] with orthoesters and the cycloaddition reaction of *o*-hydroxybenzaldehydes[117] and unsaturated alcohols in the presence of trimethyl orthoformate afforded *trans*-annelated pyrano[3,2-*c*]benzopyrans.

2.4. Peroxides

Iodine (40 mol %) promoted the transformation of geminal bishydroperoxides **80** and ketals into 1-hydroperoxy-1′-alkoxyperoxides **81** (Scheme 34); the best results were obtained in Et_2O. Analogously, the peroxides **81** were also obtained from enol ethers instead of from ketals.[257]

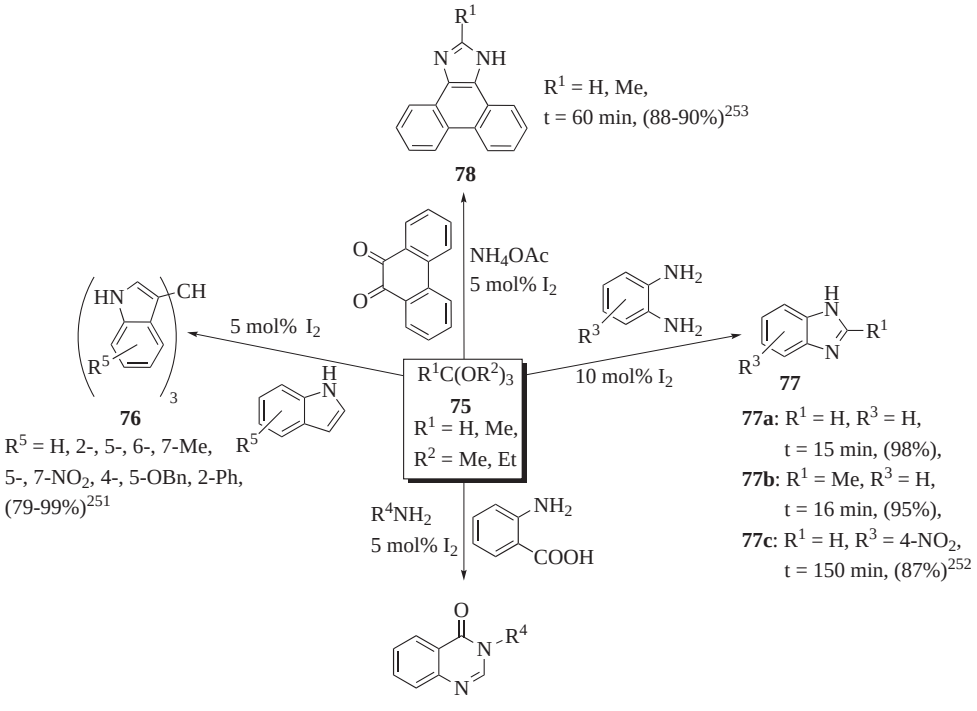


80 **81**

81a: $R^1 + R^2 = (CH_2)_5$, $R^3 + R^4 = (CH_2)_4$, R^5 = Et, (48%),
81b: $R^1 + R^2 = (CH_2)_5$, $R^3 + R^4 = (CH_2)_6$, R^5 = Et, (61%),
81c: $R^1 + R^2 = (CH_2)_6$, $R^3 = R^4 = R^5$ = Me, (64%)[257]

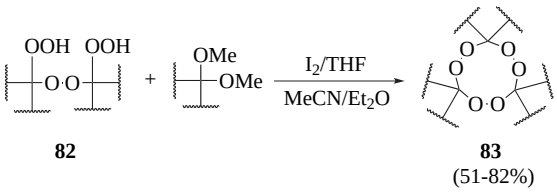
Scheme 34. IC synthesis of 1-hydroperoxy-1′-alkoxyperoxides.

Aqueous (70%) *tert*-butyl hydroperoxide (TBHP) was reported to be an efficient reagent in the oxidation of benzylic methylenes to ketones and primary amines to nitriles. A catalytic amount of iodine was necessary; in addition, pyridine was indispensable for both oxidations. Under optimized reaction conditions (1 mol % of I_2 for oxidation of benzylic methylenes, 0.5 mol % of I_2 for transformation of primary amines; equimolar amounts of pyridine relative to I_2), yields of up to 99% were obtained.[258] Bis(1-hydroperoxycycloalkyl)



Scheme 33. ICT of orthoesters.

peroxides **82** and ketals underwent **ICT** to 1,2,4,5,7,8-hexaoxonanes **83**, nine-membered cyclic triperoxides. The best results were obtained in MeCN, Et_2O and in THF (Scheme 35).[259]

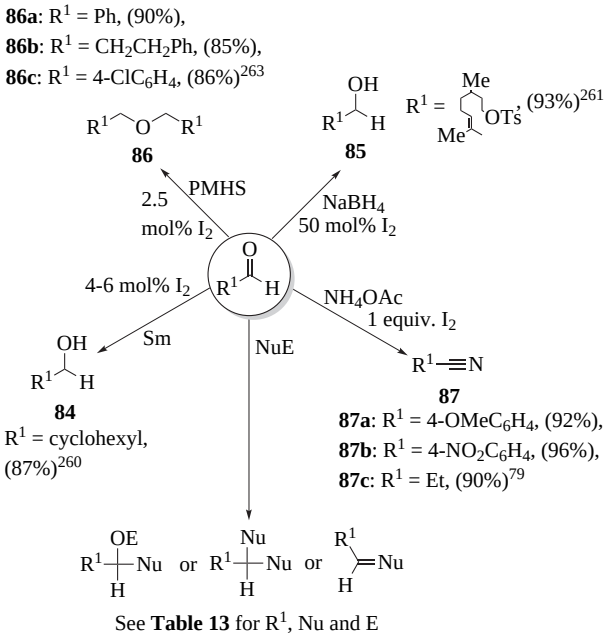


Scheme 35. **IC** synthesis of cyclic triperoxides.

3. Transformation of molecules containing sp^2 hybridized oxygen atoms bound to carbon

3.1. Aldehydes

The vast majority of **ICTs** embrace this class of substrates. Redox reactions of aldehydes are often complicated, yielding a mixture of products, although iodine has been successfully applied as a reagent or catalyst. The reduction of cyclohexanecarboxaldehyde to alcohol **84** (Scheme 36) and other aldehydes was accomplished with equimolar amounts of samarium in *i*-PrOH and a catalytic quantity of I_2 at rt. Pinacol was the side product and its formation was solvent dependent.[260]

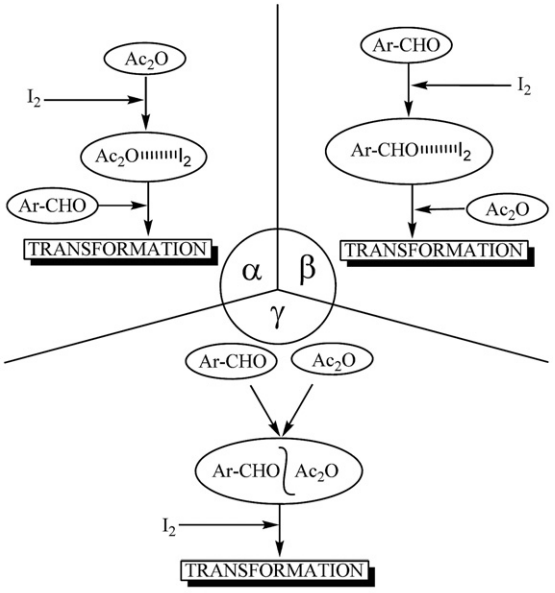


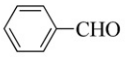
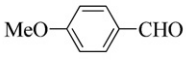
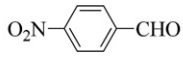
Scheme 36. Iodine-promoted redox and addition reactions of aldehydes.

With the $I_2/NaBH_4$ system, α,β-unsaturated aldehydes were regioselectively converted into the corresponding allyl alcohols **85**. Carbon-carbon double bonds, and hydroxy, ester, alkoxy, ketal, halide, tosyl and mesyl moieties remained unchanged during the transformation.[261] Iodine combined with indium was efficient in the reductive heterocyclization of 2-nitroaryl aldehydes to 2,1-benzisoxazoles.[262] Substituted aromatic aldehydes and aliphatic ketones were reductively transformed into symmetrical ethers **86** with PMHS in DCM using 2.5 mol % I_2 at rt.[263] In stoichiometric amounts, iodine was capable of oxidizing aromatic and aliphatic aldehydes into nitriles **87** in aqueous NH_4OAc[79] or aqueous NH_3.[82] The yields were excellent and no appreciable amounts of side products were formed.[79]

The transformation of aldehydes with $I_2/NaNO_2$[264] or with $I_2/PhI(OAc)_2$[265] in alcohols produced the corresponding esters in one step in good to high yields. The oxidative transformation of aldehydes and diamines into imidazoline and benzimidazole derivatives was accomplished with the $I_2/K_2CO_3/KI$ system in water[266] and with I_2/K_2CO_3 in *tert*-BuOH.[267] Iodine-mediated oxidative esterification of *ortho*-alkynyl aldehydes in methanol furnished the corresponding *ortho*-alkynyl esters, while in DCM iodocyclization took place.[268]

Iodine is known for the ability to chelate the oxygen functional groups in different modes, which may be crucial for electron-flow of the reaction. We have tested the role of the order of addition of the reactants and demonstrated that it may be of paramount importance (Scheme 37).[2]



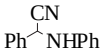
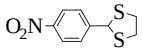
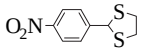
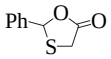
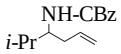
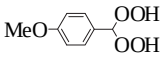
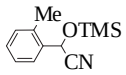
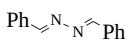
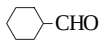
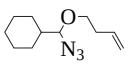
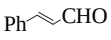
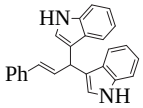
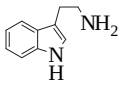
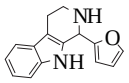
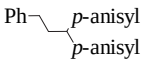
Aldehyde	Reaction protocol[a]	Conversion[c] (%)
	α	95
	β	98
	γ	97
	α	54
	β	49
	γ	32
	α	94
	β	0
	γ	0
	α[b]	67
	β[b]	66
	γ[b]	54

[a] 1 mmol of ArCHO, 1.1 mmol of Ac_2O, 0.05 mmol I_2; t = 25 min; T = 25 °C.
[b] t = 24 h.
[c] Conversion determined by ^1H NMR.

Scheme 37. Role of reaction protocol on **IC** acylation of aldehydes.

The allylation of aliphatic and aromatic aldehydes was accomplished with allyltrimethylsilane in MeCN in the presence of a catalytic quantity of iodine in short reaction time.[269] Allylation of aromatic aldehydes was also carried out with allyl bromide, tin and a catalytic amount of iodine in water, giving products in practically quantitative yield (Table 13, entry 1).[270] Sn/I_2-mediated crotylation with crotyl bromide or chloride was also performed.[270] **IC** reactions of aldehydes with amines in the presence or absence of a third participant have been widely examined.

Table 13
IC addition and addition-substitution reactions of aldehydes

Entry	Aldehyde	Substrate	I_2 (mol %)	*t*	Product	Yield (%)	Ref.
1	PhCHO		10	13 h		93	270
2	$Me(CH_2)_3CHO$	$PhNH_2$+Bu_3SnCN	10	65 min		81	273
3	PhCHO		10	30 min		99	276
4	$4\text{-}NO_2C_6H_4CHO$		10	10 min		93	275
5	$4\text{-}NO_2C_6H_4CHO$		10	4 min		93	277
6	PhCHO	$HSCH_2COOH$	10	3 h		95	280
7	$(Me)_2CHCHO$		10	15 min		74	281
8	$4\text{-}OMeC_6H_4CHO$	H_2O_2	10	5 h		76	300
9	$2\text{-}MeC_6H_4CHO$	TMSCN	20	3 min		89	282
10	PhCHO	$P(OEt)_3$	10	30 min	$PhCH(OH)PO(OEt)_2$	93	283
11	PhCHO	NH_2NH_2	100	1 min		98	284
12			10	15 min		79	116
13			20	<1 min		98	288
14			10	5 h		70	285
15	$PhCH_2CH_2CHO$	Anisole	10	72 h		76	286

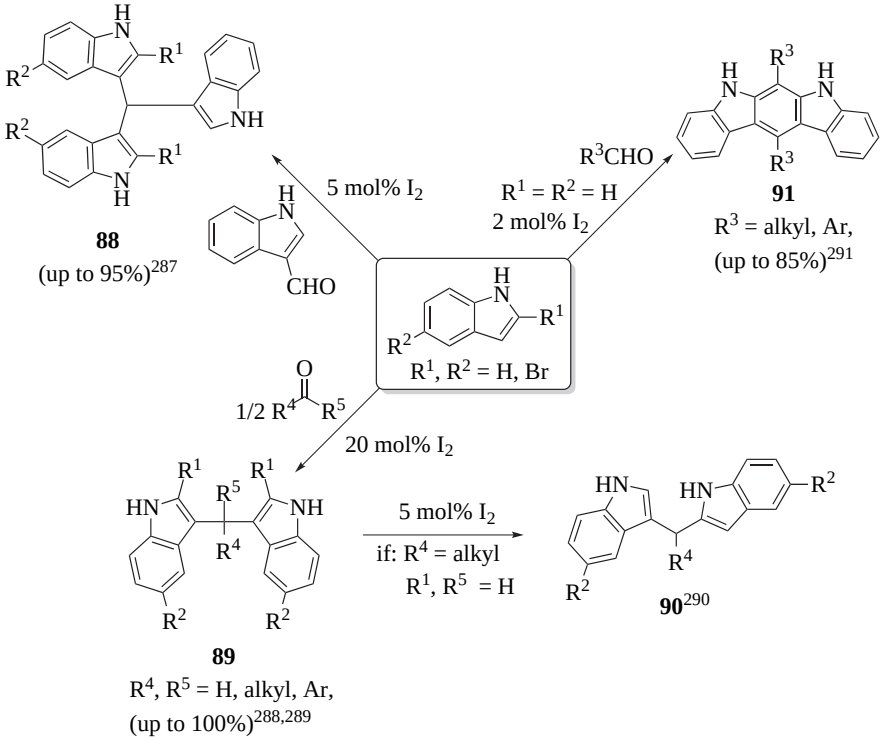
Examples include the condensation of aldehydes with 1,2-phenylenediamine, giving the benzimidazole derivatives.[271] The reaction worked well with aliphatic and aromatic aldehydes; substituents played only a minor role. An **IC** Strecker-type reaction of aromatic and aliphatic aldehydes with amines in the presence of TMSCN yielded the corresponding α-aminonitriles.[272] Besides TMSCN, the use of Bu_3SnCN was also reported. α-Aminonitriles were obtained in good yields, while carbon-carbon double bonds remained untouched (entry 2).[273] Protection of aldehydes is important in organic synthesis. Iodine was found to catalyze acetalization,[274] thioacetalization[275–277] and the formation of 1,1-diacetates[2,65] and oxathiolane[278] derivatives. Thioacetalization was widely studied with iodine in solution[276] or under SFRC with I_2 supported on Al_2O_3[275] or on natural phosphate,[277] the yields being similar in all cases (entries 3–5).

In situ-generated iodine from $Fe(NO_3)_3{\cdot}9H_2O$ and NaI was also used for the thioacetalization of aromatic aldehydes.[279] Aldehydes and mercaptoacetic acid in the presence of I_2 in IL led to the 1,3-oxathiolan-5-ones (entry 6).[280] A three-component condensation of aldehydes, benzyl carbamate and allyltrimethylsilane afforded the protected homoallylic amines in moderate yields (entry 7). The highest yield (up to 82%) was observed with aromatic aldehydes.[281] Functionalization of aldehydes often took place with TMS derivatives. In the case of TMSCN, aldehydes were transformed into the corresponding cyanohydrins (entry 9).[282] **IC** addition of triethyl phosphite to aldehydes at 80 °C in water furnished α-hydroxyphosphonates in high yields (entry 10).[283] Equimolar amounts of hydrazine hydrate, aromatic aldehyde and iodine at 0–10 °C led to the symmetrical azines within a few minutes in almost quantitative yield. EWGs increased the reactivity, while EDGs retarded it

(entry 11).[284] $TMSN_3$ in combination with alcohols transformed the aromatic and aliphatic aldehydes into the corresponding α-alkoxy azides, and or allyltrimethylsilane/alcohol combination furnished the homoallyl ethers in 70–80% yield (entry 12).[116] Iodine (10 mol %) induced the two-component Pictet–Spengler condensation of tryptamine and aromatic aldehydes to yield the tetrahydro-β-carbolines. Stereoelectronic effects of substituents on the aromatic ring of the aldehyde had a minimal effect on the product yield (entry 14).[285] **IC** Friedel–Crafts alkylation (entry 15) of electron-rich aromatics with aliphatic and aromatic aldehydes produced the desired triarylmethanes and diarylalkanes in high yield (up to 99%) in toluene at rt.[286] Analogously, **ICT** of indole-3-carboxaldehyde and substituted indoles afforded symmetrical and unsymmetrical triindolylmethanes **88** (Scheme 38).[287] Moreover,

Other non-redox **ICTs** of aldehydes include the conjugative addition of *N*-substituted indoles to α,β-unsaturated carbonyls,[294] ring expansion of β-lactams,[295–297] the synthesis of substituted quinolines via imines and aldehydes,[298,299] Prins and aza-Prins reactions,[106,292] the peroxidation of carbonyl molecules,[300] and the synthesis of nitriles with hydroxylamine hydrochloride.[301] In the peroxidation of carbonyl molecules, exemplified for 4-*tert*-butylcyclohexanone **94**, iodine was able to discriminate between hydroxy, hydroperoxy and methoxy groups and methanol, water and H_2O_2 (Scheme 40).[300]

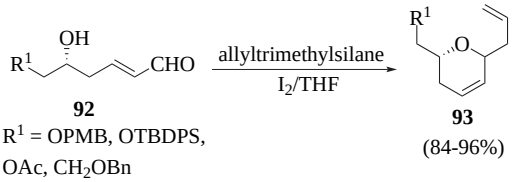
A three-component reaction of substituted aromatic aldehydes, naphthalen-2-amine and ketones in the presence of I_2 led to the corresponding benzo[*f*]quinolines **95** (Scheme 41). Increasing the ring size in the case of cyclic ketones had a minimal effect on the yield, although the reaction time lengthened.[302] **IC** transformation of aryl



Scheme 38. ICT of aldehydes and indoles.

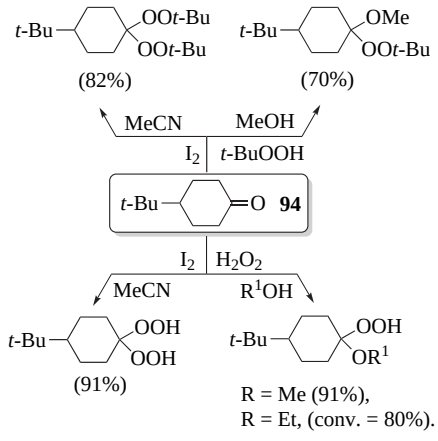
functionalization of 2 equiv of indole with 1 equiv of aryl aldehyde yielded 3,3-bis(indolyl)methanes **89**,[288,289] which further underwent two different **ICTs**. After a longer time at rt, isomerization to the 2,3′-bis(indolylmethanes) **90** took place;[290] in the case of equimolar amounts of indole and aldehyde under refluxing in MeCN in short reaction times 6,12-disubstituted 5,7-dihydroindolo [2,3-*b*]carbazoles **91** were formed (Scheme 38).[291]

The **IC** addition of aliphatic aldehydes to alkenes in DCM furnished 4-substitued 1,3-dioxanes in high yields.[292] Iodine catalyzed one-pot allylation–cyclization of δ-hydroxy-α,β-unsaturated aldehydes **92** with allyltrimethylsilane, yielding 2,6-disubstituted-3,4-dihydropyrans **93** in a highly diastereoselective manner (Scheme 39).[293]

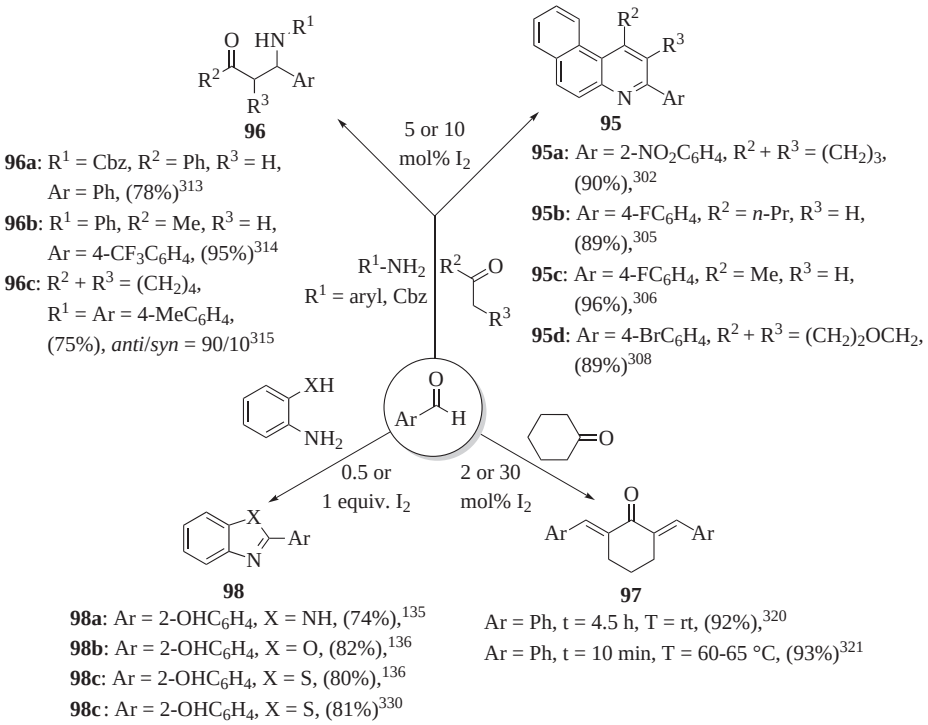


Scheme 39. IC allylation-cyclization of unsaturated aldehydes.

aldehyde, β-ketoamide and naphthaleneamine in MeCN yielded benzoquinolinamide derivatives in up to 72% yields.[303] **IC** oxidative cyclization of aryl aldehydes and α-aminoacetophenone hydrochloride furnished 2,5-disubstituted oxazoles in high yields.[304] Acyclic



Scheme 40. ICT of 4-*tert*-butylcyclohexanone.



Scheme 41. ICT of aryl-substituted aldehydes.

ketones,[305,306] 2-halo-substituted acetophenones,[307] heteroatom-containing cyclic ketones[308,309] and barbituric acid[310] were also tested, giving nitrogen heterocycles in yields of up to 96%.

Iodine served as an excellent promoter of the cyclization of aromatic aldehydes with 2-amino-4,5-dimethylthiophene-3-carboxamide to the corresponding thieno[2,3-*d*]pyrimidines in MeCN at rt.[311] Iodine was found to be an efficient catalyst for transformation of 2-amino-*N*′-arylbenzamidines with aryl aldehydes into 2,3-dihydroquinazoline analogues.[312] **ICT** of aryl aldehydes, isatoic anhydride and ammonium acetate in refluxing EtOH yielded quinazolinone and 2,3-dihydroquinazolinone derivatives.[256]

The **IC** Mannich reaction of benzyl carbamate, aromatic aldehydes and aromatic ketones produced carboxybenzyl-protected β-amino ketones **96a**. *ortho*- and *para*-Substituted benzaldehydes exhibited good reactivity, while the *meta*-substituted compounds, such as 3-methoxybenzaldehyde did not react.[313] Similarly, iodine-catalyzed (5 mol %) reactions of aldehydes, aniline and acetone furnished β-aminobutanones **96b**. EWGs on the aniline moiety decreased the reactivity, while substituents on the aldehyde had no effect on the reaction rate.[314] In the case of cyclic ketones, a noteworthy solvent effect was observed, and the *anti*/*syn* ratio of the products (**96c**) was solvent driven. The prevalent isomer was *anti*, and the best ratio was obtained in EtOH.[315] I_2/Fe/CuBr effectively catalyzed synthesis of propargylamines from aldehydes, aryl azides and alkynes.[316]

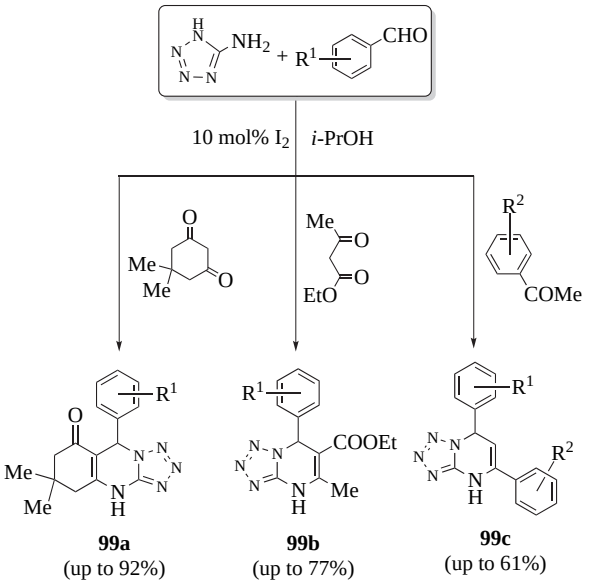
Another four-component reaction was the one-pot synthesis of β-acetamido ketones from benzaldehyde, ketone, AcCl and nitrile. AcCl was not incorporated in the product, but its presence was vital.[317,318] Iodine promoted reaction of aryl aldehyde, 2-hydroxy-1,4-naphthoquinone and 1*H*-pyrazol-5-amine derivative, giving benzo[*h*]pyrazolo[3,4-*b*]quinoline derivatives in high yields.[319] The double aldol condensation between aldehyde and ketone giving **97** took place in solution[320] or under SFRC.[321] The Claisen–Schmidt condensation of benzaldehydes and acetophenones effectively proceeded in dry dioxane[322] in the presence of 5 mol % of I_2, yielding the corresponding chalcones; the transformation was also performed under SFRC.[323] Analogously, I_2-catalyzed aldol condensation of 1-carbethoxy-4-piperidone with aldehydes in MeCN at rt led to the α,α′-bis(substituted benzylidene)cycloalkanones.[324] An aqueous solution of KI/I_2 was an efficient catalyst for the condensation of aromatic aldehydes and active methylene compounds, giving *E*- substituted alkenes.[325] **IC** Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate afforded ethyl α-cyanocinnamates.[326] I_2 was an efficient catalyst for the condensation of rhodanine with aromatic aldehydes by grinding at rt under SFRC, producing 5-(arylbenzylidene)rhodanines in very good yields.[327] Aromatic aldehydes, anilines and homophthalic anhydride underwent **IC** one-pot transformation into tetrahydroisoquinoline-4-carboxylic acids with high cis selectivity.[328] Iodine-catalyzed cyclocondensation of salicylaldehydes with 2,2-dimethoxypropane in DCM at rt furnished a substituted 2*H*-1-benzopyran framework.[329]

Iodine catalyzed the cyclization of *ortho*-substituted anilines with aryl aldehydes. Depending on the *ortho* substituent, the corresponding benzimidazole, benzoxazole or benzothiazole derivatives **98** were formed. Benzothiazoles were obtained at rt[136] and 100 °C,[330] while benzoxazoles and benzimidazoles required MW irradiation or elevated temperature.[135,136] **IC** transformation of aryl aldehydes and hippuric acid in the presence of Ac_2O effectively afforded azalactones under MW irradiation in short reaction times.[331]

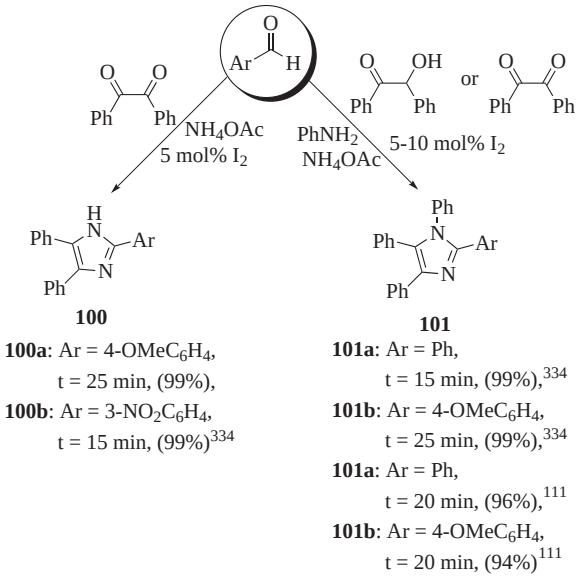
An **IC** multicomponent reaction of aryl aldehydes, 5-aminotetrazole and a second carbonyl molecule furnished a library of tetrazolo[1,5-*a*]pyrimidine analogues **99a–c** (Scheme 42).[332]

Different synthetic strategies for the synthesis of the imidazole ring were explored. Thus, 2,4,5-triarylimidazoles **100** were obtained in the condensation of benzoin,[115] or benzil,[333,334] NH_4OAc and benzaldehydes; a further addition of amine resulted in the formation of 1,2,4,5-tetraarylimidazoles **101** (Scheme 43).[111,334] It was established that iodine facilitated the aerial oxidation of benzoin to benzil before cyclization occurred.[111,115]

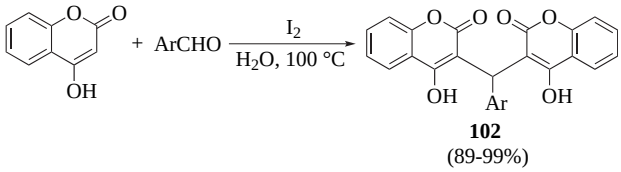
Several other iodine-promoted condensations to form heterocycles were reported,[335–342] including symmetrical[343–345] and unsymmetrical[346] *meso*-porphyrin skeletons and *meso*-substituted



Scheme 42. **IC** synthesis of tetrazolo[1,5-*a*]pyrimidine derivatives.



Scheme 43. **IC** synthesis of arylimidazoles.



Scheme 44. **IC** synthesis of bis(4-hydroxycoumarine)methanes.

dipyrromethanes[347] from pyrrole and benzaldehydes, and the tandem cyclization-cycloaddition reaction of *ortho*-alkynyl-substituted benzaldehydes to polyoxacyclic ring systems.[348]

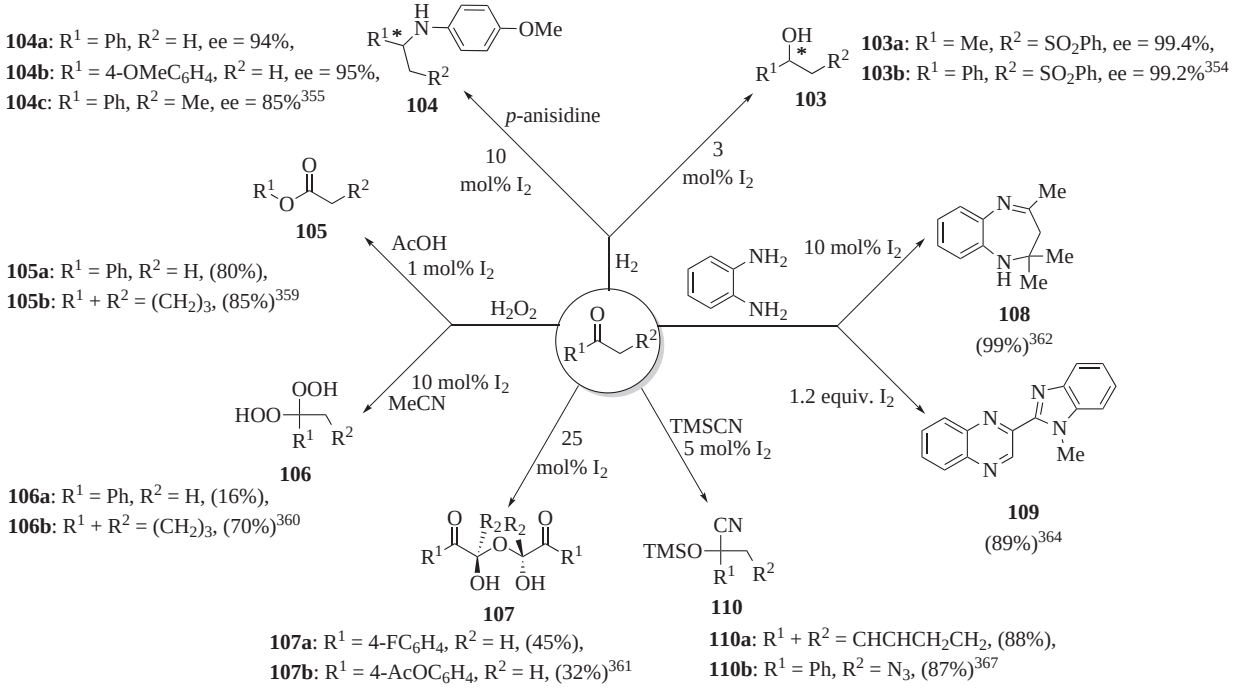
ICT of benzaldehydes, pyrazolone analogues and indoles led to triarylmethane derivatives;[349] furthermore, aromatic or hetero-aromatic aldehydes with 4-hydroxycoumarin or dimedone in water furnished bis(4-hydroxycoumarin)-substituted methane derivatives **102** in excellent yields (Scheme 44).[350]

Samarium metal and iodine in refluxing MeOH promoted the reductive cyclization of aldehydes with substituted *o*-nitrobenzamides or *o*-azidobenzamides into 2,3-dihydro-4(1*H*)-quinazolinone analogues.[351] Iodine effectively catalyzed the Barbier reaction of aldehydes with alkylsamarium halides in THF.[352] Sm/I_2 or $Sm/I_2/Ti(i\text{-}OPr)_4$ in MeOH at rt promoted pinacol formation from aldehydes in good yields.[353] The remaining reactions of aldehydes with other substrates are covered in previous and the following sections.

3.2. Ketones

Ketones have participated in numerous **IC** reactions. β-Sulfonyl ketones were enantioselectively hydrogenated in the presence of I_2 and chiral ruthenium catalysts to hydroxy sulfones **103** (Scheme 45). Although hydrogenation proceeded with Ru(II) complexes without I_2, the former was added to improve the reactivity and enantioselectivity.

The functionalizations of aromatic β-sulfonyl ketones bearing different substituents were quantitative in all cases, the ees being above



Scheme 45. **ICT** of ketones.

97% and the electronic effects having little effect on the enantioselectivity.[354] Another reported asymmetric hydrogenation was the **IC** reduction of in situ-generated imines from aryl ketones and *p*-anisidine in the presence of $Ti(i\text{-}OPr)_4$ and an iridium chiral catalyst to the amines **104**. Quantitative conversions were achieved and *p*-EDGs on the aryl ketone increased the stereoselectivity, while increasing steric hindrance of the R^2 group noticeably reduced it (Scheme 45).[355] Metallic samarium in combination with I_2 promoted the formation of benzoins from benzophenones and, in some cases, benzil was formed.[356]

Iodine has played an important role in the oxidation of carbonyl molecules as a catalyst and also as a reagent. Oxidation of aldehydes and ketones with an excess of iodine in MeOH under basic conditions furnished α-hydroxy ketals and α-hydroxy acetals in 50–89% yields.[357] Oxidation of ketones to α,β-unsaturated esters in alkaline media seemingly involved two iodination steps and a Favorskii-type rearrangement.[358] Next, a Baeyer–Villiger oxidation of aromatic and aliphatic ketones with an I_2/H_2O_2 (40%) system in acetic acid to esters and lactones **105** and aldehydes to acids was reported.[359] The transformation of aliphatic ketones with an I_2/H_2O_2 system in MeCN produced geminal dihydroperoxides **106**; aromatic ketones exhibited poor reactivity (Scheme 45, **106a**).[300,360] Acetophenones were converted into hemialdals **107** in yields of up to 53%; the oxidation was highly stereoselective, giving only a single stereoisomer.[361] Cyclocondensation of *o*-phenylenediamine and ketones yielded 1,5-benzodiazepine **108** and quinoxaline **109** derivatives in solution or under SFRC; 10 mol % of I_2 was required for the synthesis of **108**[362,363] and more than 1 equiv of I_2 was needed for the generation of **109**.[364]

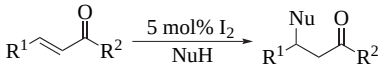
Iodine promoted a selective scission of the C-17-dihydroxyacetone moiety of corticosteroids with an excess of 35% aqueous NH_3 in MeCN, giving 17-ketosteroids in good yields.[365]

Enolizable ketones could be converted into the corresponding α-thiocyanato ketones by means of ammonium thiocyanate and equimolar amount of iodine in refluxing MeOH; in situ-formed $(SCN)_2$ was proposed as the reactive species.[366]

Typical for ketones are nucleophilic additions; I_2 selectively catalyzed the 1,2-addition of TMSCN to saturated and α,β-unsaturated ketones, affording cyanohydrin trimethylsilyl ethers **110** within 40 min.[367]

Nitro or azido aromatics underwent a reductive cyclization with ketones in the presence of samarium and catalytic amounts of I_2, producing quinazolinone derivatives.[351] Samarium metal and I_2 successfully promoted Barbier reactions of ketones, giving tertiary alcohols.[352] Aryl-substituted ketones underwent reduction to the alkane derivatives by means of H_3PO_2 and iodine.[368] **IC** cyclization of α-bromoacetophenones with *N*-substituted ureas in EtOH produced 2-aminothiazole derivatives.[369] Reductive dimerization of α-halogenated ketones with zinc in dry THF that yielded the related 1,4-diketones was promoted by catalytic amounts of iodine.[370] Other **IC** cyclization reactions involving ketones are the syntheses of quinolines **111**,[371,372] dihydroquinolinones **112**,[373] quinazolin-4(1*H*)-ones **113**,[374] and 2-arylquinazolines **114**[375,376] (Scheme 46), cycloadditions to substituted *trans*-cyclobutanes,[377] Pictet–Spengler cyclization with tryptamine,[378] Bohlmann–Rahtz synthesis of 2,3,6-trisubstituted pyridines[379] and the synthesis of phenanthrimidazole derivatives.[253] **IMT** of *p*-hydroxyacetophenone and excess of thiourea under SFRC produced 2-amino-4-(*p*-hydroxyphenyl) thiazole.[380]

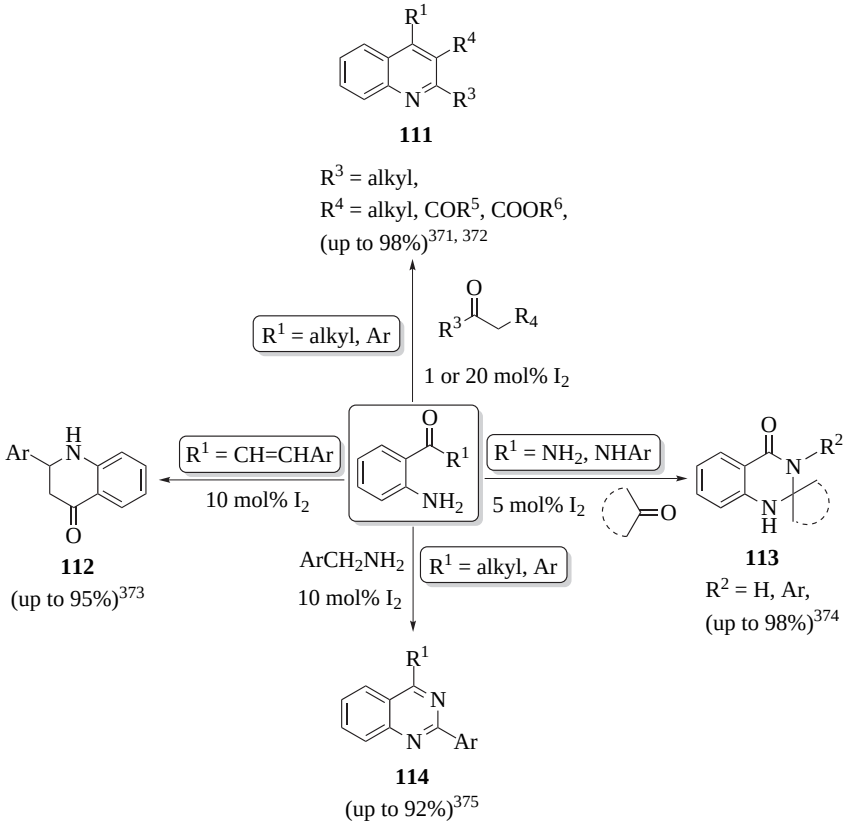
Michael addition of indoles and thiols[381] to α,β-unsaturated ketones **115**[382,383] procedeed in solution and under SFRC, giving 1,4-adducts **116** (Scheme 47). The reaction of pyrrole and



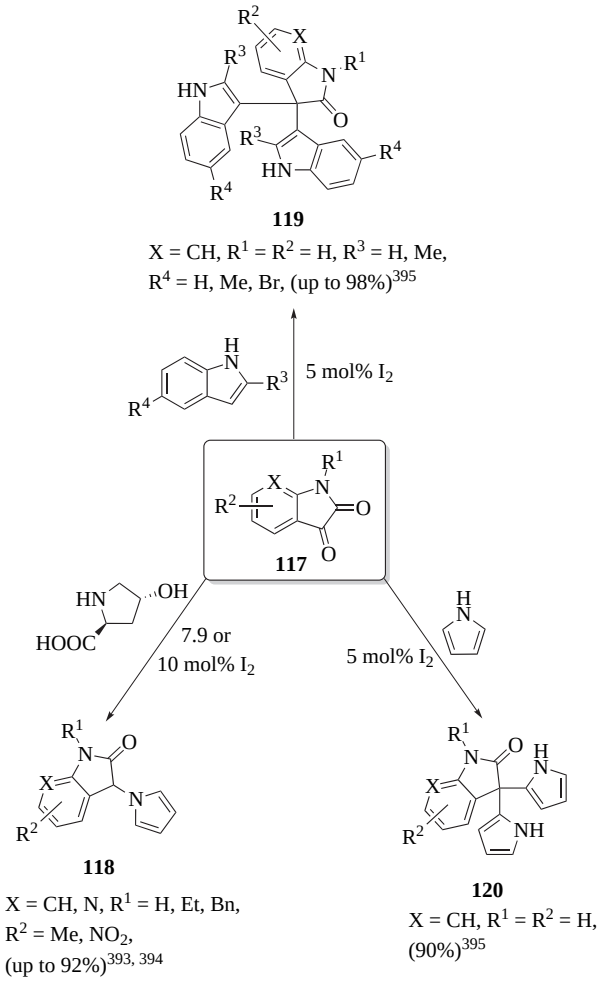
115 **116**

R^1 = H, alkyl, R^2 = alkyl, Ph, $R^1 + R^2$ = cycloalkyl,
Nu = thioalkyl, thioaryl, 3-indolyl,
t = 3-30 min, (45-97%)[381,382]

Scheme 47. IC Michael addition to α,β-unsaturated ketones.



Scheme 46. IC formation of heterocyclic molecules.



Scheme 48. **IC** functionalization of isatins.

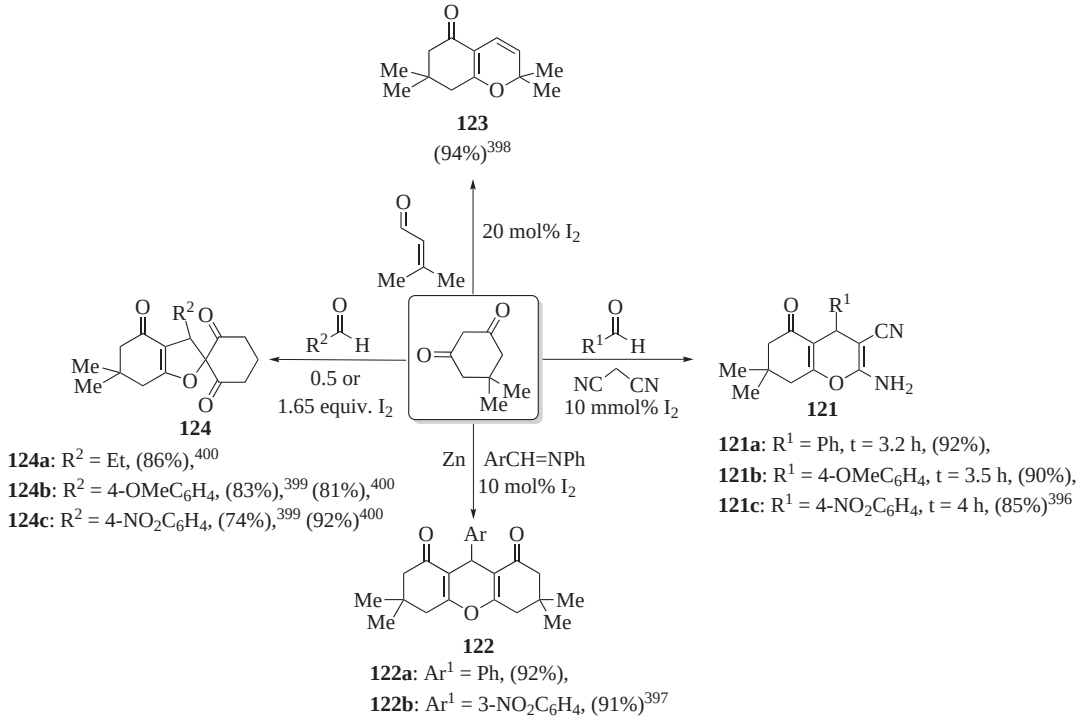
α,β-unsaturated ketones led to a mixture of the 2-alkylpyrrole and 2,5-dialkylpyrrole; the latter was the exclusive product when a twofold excess of ketone was used.[384] Iodine in refluxing DMSO catalyzed the dehydrogenation of 2′-hydroxychalcones to the corresponding flavone, chromone and thiochromone derivatives;[385] a similar observation was reported with the *O*-allyl ethers.[199]

The additions of *N*-substituted indoles to doubly conjugated systems, 1,5-diaryl-1,4-pentadien-3-ones, were also studied. Ultrasound promoted the Michael addition in MeCN in the presence of I_2 and yielded a mixture of mono and bis adducts; the ratio was strongly dependent on the quantity of I_2.[386] Catalytic amounts of I_2 and a higher temperature favoured the 1,4-addition of TMSCN to β-alkoxyvinyl alkyl ketones, while the basic catalyst and rt favoured the 1,2-addition.[387,388] **IC** 1,4-conjugate addition of allyltrimethylsilane to α,β-unsaturated ketones produced allyl-substituted ketones with high selectivity.[389] Diaryl-1,4-pentadien-3-ones reacted with indole in dry EtOH in the presence of 20 mol % of I_2, forming bis(3-indolyl)methylarenes.[390]

IC nucleophilic additions of furan, pyrrole, thiophene and indole to acetone have been examined theoretically. Computational studies revealed the importance of complexation between the carbonyl oxygen and iodine and that the first iodine molecule bound to the substrate maximally diminishes the energy barrier by 41 kJ/mol. The C2 addition is more favourable for furan, pyrrole and thiophene; in contrast, the C3 site is preferred for indole.[391,392]

Other **IC** transformation of ketones include the coupling of isatins **117** with 4-hydroxyproline to indolin-2-ones **118**[393,394] or substituted indoles and pyrrole to 3,3-diheteroaryloxindoles **119** and **120**[395] (Scheme 48) and the reactions with acetals, alcohols, aldehydes, enol ethers, phenols and ketoesters, which have already been mentioned in previous sections or will be described in the following sections.

3.2.1. Diketones. Iodine promoted several cyclizations of 1,3-diketones, especially dimedone, which was often used in such transformations. Tetrahydrobenzo[*b*]pyrans **121** (Scheme 49) were synthesized from an equimolar mixture of dimedone, aromatic aldehydes and malononitrile in the presence of 10 mmol % of I_2 in DMSO.[396] Condensation of dimedone with imines yielded

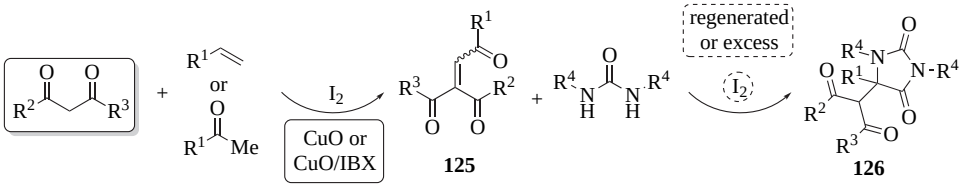


Scheme 49. **ICT** of 1,3-diketones.

xanthenediones **122** and, noticeably, these products were obtained only with I_2/Zn in MeOH.[397]

Dimedone and other 1,3-dicarbonyl compounds underwent **IC** Knoevenagel condensation with α,β-unsaturated aldehydes, followed by 6π-electrocyclization to 2*H*-pyrans **123** in high yields.[398] I_2/NH_4OAc-mediated transformation of dimedone and aldehydes in MeOH furnished spirodihydrofurans **124**,[399] the same products were obtained in a ball-mill in the presence of I_2/DMAP.[400] Reaction of 1,3-indanedione with aldehydes under the mechanical milling conditions accomplished the unexpected bis-spiro-substituted cyclopropane derivatives. Aromatic aldehydes bearing EWGs gave higher yields than those having EDGs.[400] The condensation of aliphatic and aromatic 1,2-dicarbonyl molecules with aromatic 1,2-diamines furnished the quinoxaline scaffold; reactions were performed in MeCN[401] in DMSO[402] and in aqueous EtOH.[403] Yields were practically the same, but the reaction in MeCN was faster. **IC** condensation of benzil, aliphatic amine or benzylamine and benzonitrile under SFRC yielded 1,2,4,5-tetrasubstituted imidazoles in high yields.[404]

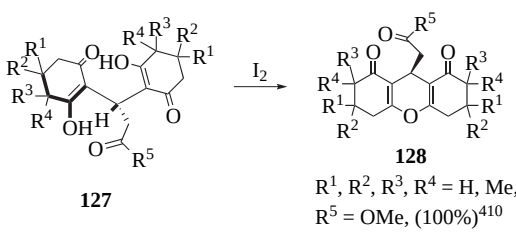
ICTs of β-ketones or β-ketoesters to β-enamino derivatives were reported. The reaction was completed in less than a minute under SFRC; from symmetrical diamines, dimeric products were obtained.[405] The functionalization of 1,3-diketones with alcohols led to the corresponding β-keto enol ethers in high yields. Increasing steric hindrance of the alcohol exerted a negative effect on the reactivity.[406] The condensation of methyl ketones or terminal aryl alkenes with 1,3-dicarbonyl molecules to (*E*/*Z*)-1,4-enedione derivatives **125** with *E* prevalence proceeded with I_2 in DMSO.[407] This domino process was further integrated with the second domino process in one flask; excess or in situ regenerated iodine served as a catalyst for transformation of **125** with ureas to the corresponding hydantoins **126** (Scheme 50).[408]



Scheme 50. IC preparation of tricarbonyl compounds and hydantoins.

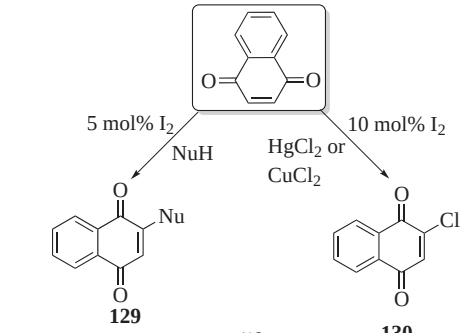
Carbostyril derivatives and dimedone underwent **IC** cyclization with anilines or 1-amino-1,3,4-triazole and sulfur furnishing thiazine and thiadiazine derivatives. The reaction proceeded best in THF, while US activation proved superior over thermal methods.[409] Tandem Michael/Michael adducts **127** underwent **IC** cyclization to 9-substituted-1,8-dioxooctahydroxanthenes **128**[410] (Scheme 51); furthermore, iodine in high amounts initiated an unusual intramolecular carbocyclization of 2-benzyl-2,4,5-trichlorocyclopent-4-ene-1,3-dione, which afforded 2,3,3a,8a-tetrachloro-8,8a-dihydrocyclopenta[*a*]inden-1-one in a low yield (~15%).[411] **IC** hydroalkylation of 1,3-diketones with alkenes in toluene at 110 °C furnished α-substituted-1,3-diketones in good yields.[412]

IC photochemical oxidative decarboxylation of 1,3-diketones afforded 1,2-diketones in dry EtOAc in the presence of $Ca(OH)_2$.[413] **ICTs** of 1,4-diketones are scarce and, to our knowledge, the only known reaction is the cyclization of diketones with aliphatic and aromatic amines to pyrroles in THF.[414,415]



Scheme 51. IC cyclization of bis-cyclohexenone derivatives.

3.2.2. Quinones. **IC** conjugative addition of primary and secondary aliphatic and aromatic amines to 1,4-naphthoquinone furnished the 2-amino derivatives **129** (Scheme 52); yields ranged between 17 and 86%.[416] US-promoted transformation in EtOH was completed within 2 h; EWGs on indoles drastically reduced the reactivity.[417]



129a: Nu = NHBn, (84%),[416]
129b: Nu = NHBu, (55%),[416]
129c: Nu = 3-indolyl, (57%)[417]

Scheme 52. ICT of 1,4-naphtoquinone.

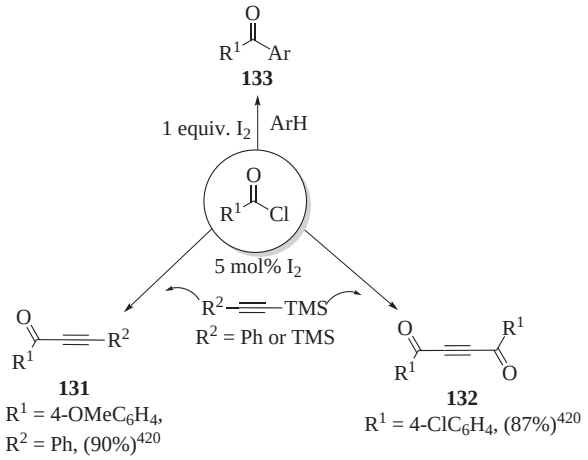
IC chlorination of naphthoquinones with a $CuCl_2/HgCl_2$ mixture in acetic acid afforded the chlorinated naphthoquinones **130** in good yields.[418] Iodine in combination with $InCl_3$ successfully catalyzed [3+2] stereoselective cycloaddition reactions of 1,4-benzoquinones and alkenes, yielding *trans* 2,3-dihydrobenzofurans.[377]

The I_2/H_2O_2 system in MeCN was employed in ring contraction of 1,2-quinones, affording the cyclopentyl and fluorenone derivatives; the reaction is limited to *o*-quinones.[419]

3.3. Acyl chlorides

Besides the already mentioned ring-opening reactions of ethers,[188,189] acyl chlorides underwent coupling with alkynylsilanes; 1.2 equiv of acyl chloride and 1 equiv of alkylnyltrimethylsilane in the presence of 5 mol % of I_2 produced alkynyl ketones **131**; 1,4-diketoalkynes **132** were formed when 2 equiv of bis(trimethylsilyl) acetylene was used.[420] Acyl chlorides have been further applied in a Friedel–Crafts acylation of aromates catalyzed with an I_2/DMF system. Acylation of anisole with AcCl and PhCOCl gave **133a** and **133b** (Scheme 53). Functionalization was highly *para* regioselective, yielding only traces of the *ortho*-substituted product (3%), although the transformation took place at 140 °C. Di- and tri-methoxy-substituted arenes gave products in moderate yields (**133c** and **133d**), while deactivated arenes failed to react.[421] Aromatic and aliphatic amines were protected using benzyloxycarbonyl chloride (Cbz-Cl) in MeOH with 2 mol % of I_2. The amine group was chemoselectively protected, even in the presence of an alcohol, phenol or thiophenol moiety.[422] **IC** nucleophilic substitution of acetyl or benzoyl chloride with amines and *N*-heterocycles yielded the corresponding *N*-acylated derivatives under SFRC.[423]

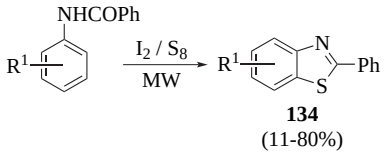
133a: R^1 = Me, Ar = 4-$OMeC_6H_4$, (67%),
133b: R^1 = Ph, Ar = 4-$OMeC_6H_4$, (81%),
133c: R^1 = Ph, Ar = 1,2-$(OMe)_2C_6H_3$, (72%),
133d: R^1 = Ph, Ar = 1,2,3-$(OMe)_3C_6H_2$, (58%)[421]



Scheme 53. ICT of acyl chlorides.

3.4. Amides

Iodine catalyzed (10 mol %) the oxidative cyclization of benzanilides with sulfur to the 2-phenylbenzothiazole derivatives **134** under MW irradiation in solution or under SFRC (Scheme 54).[424]

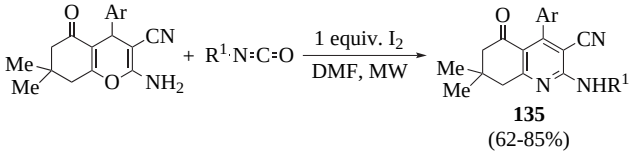


Scheme 54. IC synthesis of benzothiazoles.

Benzylamides were transformed into *N*-acyl- and *N*-aroylbenzamides with molecular oxygen in the presence of 1 mol % of I_2 under illumination with a 500-W xenon lamp in dry EtOAc.[425]

3.5. Isocyanates

IMT of isocyanates and 2-aminochromene-3-carbonitriles under MW irradiation at 150 °C in DMF afforded 2-aminoquinoline-3-carbonitrile **135** derivatives in good to high yields (Scheme 55).[426]



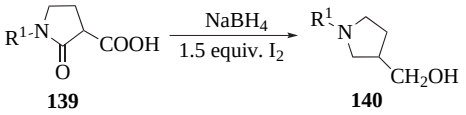
Scheme 55. IMT of isocyanates and chromene derivatives.

4. Transformation of molecules containing sp^2 and sp^3 hybridized oxygen atoms bound to carbon

4.1. Acids

Carboxylic acids participated in **IC** redox reactions. Reductive acylation of nitroarenes in the presence of red phosphorus as a reducing agent yielded *N*-arylamides **136**; the best selectivity was obtained using 4 mol % of I_2.[427] A combination of I_2/$PhI(OAc)_2$ promoted a fragmentation–recombination reaction of α-amino acids with enol silyl ethers to the corresponding β-amino acid derivatives **137** (Scheme 56).[428] **IC** aerobic photodecarboxylation of α-hydroxy carboxylic acids yielded carboxylic acids **138**. Optimal yields were achieved with 5 mol % of I_2; an increase in the amount of iodine inhibited the oxidation, and ethyl acetate was found to be the solvent of choice.[429]

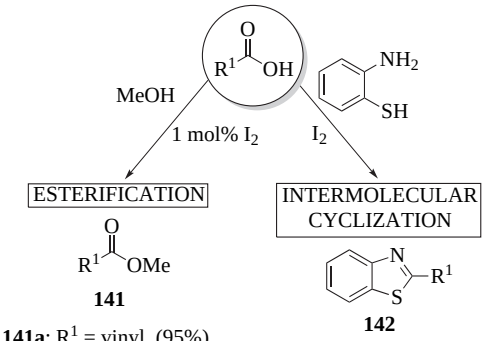
Reduction of carboxylic acids, esters and amides with an I_2/$NaBH_4$ system has been reported;[430] moreover, *N*-aryl-γ-lactam 2/3-carboxylic acids **139** were converted into (*N*-aryl-pyrrolidine-2/3-yl)-methanols **140**; the substituent effects were insignificant (Scheme 57).[431,432]



140a: R^1 = 4-MeC_6H_4, (76%),
140b: R^1 = 4-BrC_6H_4, (81%)[431,432]

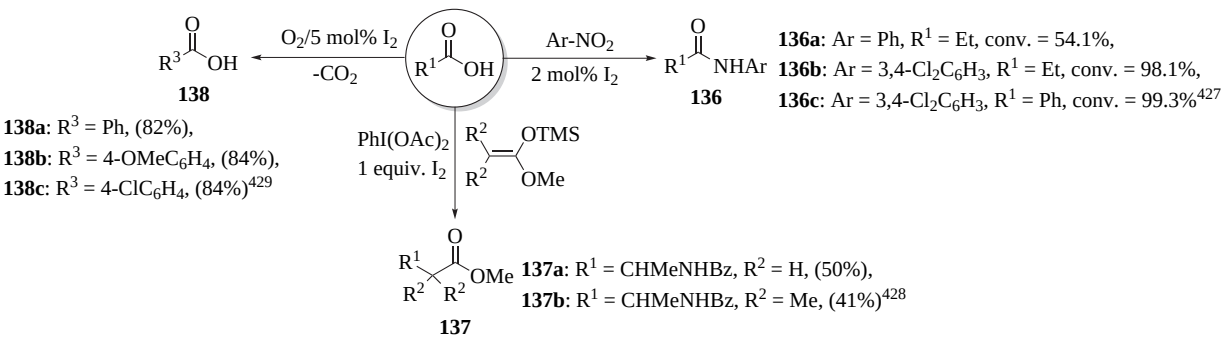
Scheme 57. IC reduction of *N*-aryl-γ-lactam 2/3-carboxylic acids.

Furthermore, iodine was capable of catalyzing esterification reactions. Acids underwent **IC** esterification in the presence of a large excess of alcohol, furnishing the esters **141** (Scheme 58). Aliphatic acids reacted well, while benzoic acids failed to react.[62]



141a: R^1 = vinyl, (95%),
141b: R^1 = Bn, (95%),
141c: R^1 = $CH_2(CH_2)_{15}Me$, (98%)[62]

Scheme 58. IC esterification and cyclization reactions of carboxylic acids.



138a: R^3 = Ph, (82%),
138b: R^3 = 4-$OMeC_6H_4$, (84%),
138c: R^3 = 4-ClC_6H_4, (84%)[429]

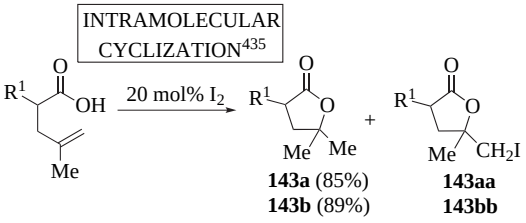
136a: Ar = Ph, R^1 = Et, conv. = 54.1%,
136b: Ar = 3,4-$Cl_2C_6H_3$, R^1 = Et, conv. = 98.1%,
136c: Ar = 3,4-$Cl_2C_6H_3$, R^1 = Ph, conv. = 99.3%[427]

137a: R^1 = CHMeNHBz, R^2 = H, (50%),
137b: R^1 = CHMeNHBz, R^2 = Me, (41%)[428]

Scheme 56. IC redox reactions of carboxylic acids.

Later, we showed that benzoic acid could be esterified with 1-phenylethanol under SFRC.[48] Esters could also be prepared from carboxylic acids in the ring-opening reactions of epoxides.[110,234]

Benzothiazole derivatives **142** were synthesized from carboxylic acids and 2-aminothiophenol under SFRC in the presence of 10 mol % I_2, although no yield was given.[433] SFRC was also the most suitable for the Michael addition of thiols to α,β-unsaturated carboxylic acids.[434] **IC** lactonization of γ-methyl-γ,δ-pentenoic acids to γ,γ-dimethyl-γ-butyrolactones **143** in DCM occurred readily; trace amounts of iodinated products were also formed (Scheme 59).[435] Intermolecular cyclization of α-hydroxy carboxylic acids with aldehydes in THF was also accomplished, producing dioxolanones.[99] **IC** chemoselective N-formylation of aliphatic and aromatic amines with formic acid took place at 70 °C with neat reactants.[436]

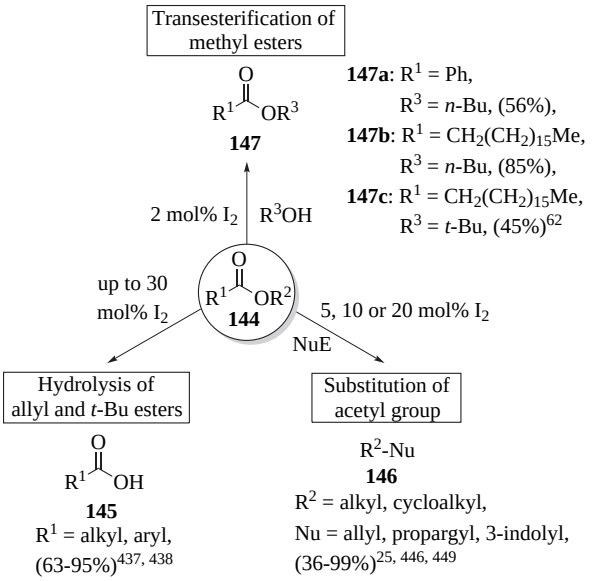


143a, 143aa: R^1 = *n*-Bu,
143a/**143aa** = 97/3,
143b, 143bb: R^1 = Bn,
143b/**143bb** = 98/2

Scheme 59. IC of unsaturated acids to lactones **143**.

4.2. Esters

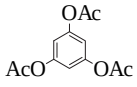
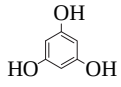
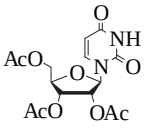
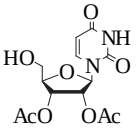
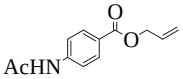
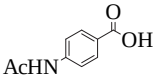
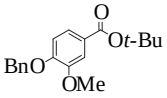
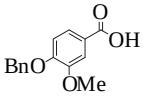
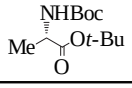
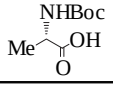
Various **ICTs** of esters **144** were studied (Scheme 60). Deprotection of allyl carboxylic esters was efficiently catalyzed with the I_2/DMSO couple, giving the acids **145** (Table 14, entry 6), the method working well with both aliphatic and aromatic carboxylic acid allyl esters.[437] Hydrolysis of *tert*-Bu esters in MeCN took place in the presence of I_2, furnishing **145**, with groups like *N*-Boc, OBn and acetate remaining unaffected.[438] **IC** conjugative addition of aliphatic and aromatic amines to α,β-unsaturated esters; the former reacted at rt in DCM, the latter required refluxing toluene.[439]



Scheme 60. ICT of esters.

The hydrolysis of aromatic acetates was realized with I_2/MeOH, giving hydroxy substituted products (Table 14, entries 1 and 2). Alkyl acetates, esters, ethers and lactones remained intact.[440] Fully acetylated nucleosides and carbohydrates were selectively deprotected on the primary carbon atom (Table 14, entry 3),[441] while glycerol esters underwent hydrolysis at 60 °C with an I_2/MeOH system.[198] Transesterification of soybean oil (fatty-acid triglycerides) in MeOH to biodiesel (fatty-acids methyl esters) was performed with an I_2/Zn catalyst. The reaction with iodine alone gave the product in low yield.[70] **IC** transesterification with other alcohols (e.g., *i*-PrOH and *tert*-BuOH) was carried out; methyl esters were easily converted into

Table 14
IC hydrolysis of esters

Entry	Substrate	I_2 (mol %)	*t*/*T* (°C)	Product	Yield (%)	Ref.
1		39	4 h/rt		85	440
2	4-$OMeC_6H_4OAc$	39	3 h/rt	4-$OMeC_6H_4OH$	92	440
3		293	14.5 h/68		69	441
4	4-$OMeC_6H_4COOCH_2CHCH_2$	—[a]	30 min/130	4-$OMeC_6H_4COOH$	75	437
5	4-$NO_2C_6H_4COOCH_2CHCH_2$	—[a]	20 min/130	4-$NO_2C_6H_4COOH$	95	437
6		—[a]	30 min/130		78	437
7		30	3 h/Reflux		85	438
8		30	5 h/Reflux		86	438

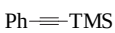
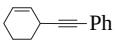
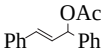
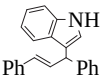
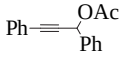
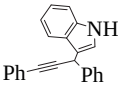
[a] Not reported.

tert-butyl esters **147c**, but transesterification with benzyl alcohol did not proceed.[62]

Metallic samarium and iodine were utilized for deacylation and dealkyloxycarbonylation of esters and lactams; the transformation was chemoselective.[442] Iodine catalyzed the preparation of allylsamarium bromide from allyl bromide and samarium. Efficient direct geminal diallylation of lactones, lactams and acyclic amides was accomplished in high yields and short reaction times.[443] A stereoselective dimerization of phenylacetic esters and amides was performed electrochemically in the presence of a pyrrolidone base and iodine.[444] Iodine promoted the highly effective transformation of selenol esters into symmetrical diselenides in dry MeOH.[445]

IC substitution of the ester group in cyclic allylic acetates with allyl (Table 15, entry 1) and alkynyl groups (Table 15, entry 2)[446] was reported. Benzyl acetates were also suitable for allylation (Table 15, entry 5).[25]

Table 15
IC nucleophilic substitutions of esters

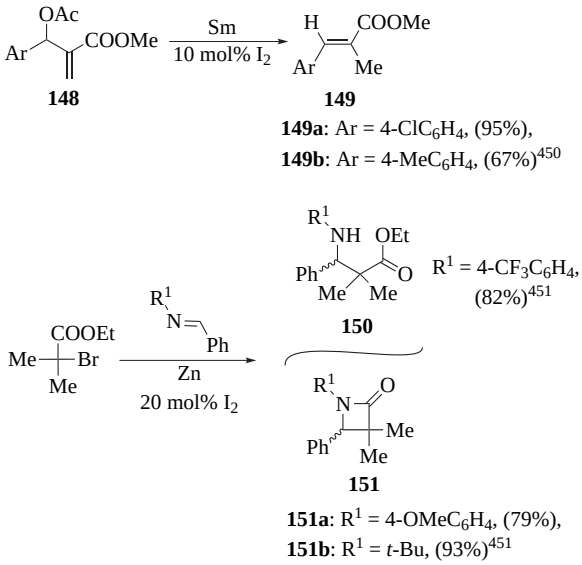
Entry	Substrate	NuE	I_2 (mol %)	t[a]	Product	Yield (%)	Ref.
1			5	30 min		82	446
2			5	35 min		75	446
3			5	20 min		95	449
4			20	3 h		69	449
5			10	90 min		87	25

[a] All experiments at rt.

D-ribonucleotides were prepared from 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose and nucleobases in the presence of an excess of HMDS and I_2 doped on the natural phosphate.[447] HMDS and I_2/natural phosphate were utilized for the selective, one-pot synthesis of antiviral nucleosides.[448] Substitution took place on the anomeric position, affording both stereoisomers; pyrimidine bases reacted at the *N*-1 position only; in the case of purine bases, the reaction regioselectively took place at *N*-9. Substitution of the acetate group was studied in the **ICT** of indoles with allylic (Table 15, entry 3) and propargylic acetates (Table 15, entry 4). Allylation worked with 5 mol % of I_2 while propargylation required 20 mol % of I_2; allylation was much faster than propargylation.[449]

Baylis–Hillman adducts **148** could be reductively deacetylated with the Sm/I_2 couple (Scheme 61) to the corresponding (*E*)-methyl cinnamic esters **149**. Reaction in the presence of higher amounts of I_2 selectively led to iodinated ester products.[450]

IC Reformatsky reactions of α-bromoesters with imines in the presence of zinc dust under US was reported. Electronic effects markedly influenced the outcome; β-amino esters **150** were formed if the anilino moiety contained an EWG, while β-lactams **151** were generated if an EDG was attached. Moreover, the method was not limited to *N*-aryl amines (Scheme 61).[451] Other transformations, in which the ester group remained intact during the process, were also reported, e.g., conjugative addition of silyl ketene acetals to α,β-unsaturated lactones[452] or allylation and cyanation of aza-aromatics.[453] A lanthanum metal, TMSCl, CuI and iodine system proved to be effective in the deoxygenative dimerization of esters to hydrocarbons.[88,89]



Scheme 61. **ICT** of esters.

4.2.1. Ketoesters. Ketoesters **152** took part in numerous **IC** cyclization reactions. Several varieties of cyclizations of β-ketoesters with aromatic or aliphatic aldehydes and urea or thiourea to form substituted 3,4-dihydropyrimidin-2(1*H*)-ones **153** (Scheme 62) were described. Transformation was carried out in MeCN solution (Table 16, entry 1)[454] and toluene (Table 16, entry 2).[455] MW irradiation under SFRC was utilized with I_2 adsorbed on neutral alumina (Table 16, entries 3 and 4),[456] while classical heating required longer reaction times (Table 16, entry 5).[457] US proved to be less effective and the yields were somewhat lower (Table 16, entry 6).[458] Derivatization of *N*-(3-chloro-4-fluorophenyl)urea led to 3,4-dihydropyrimidin-2(1*H*)-ones possessing antimycobacterial activity.[459]

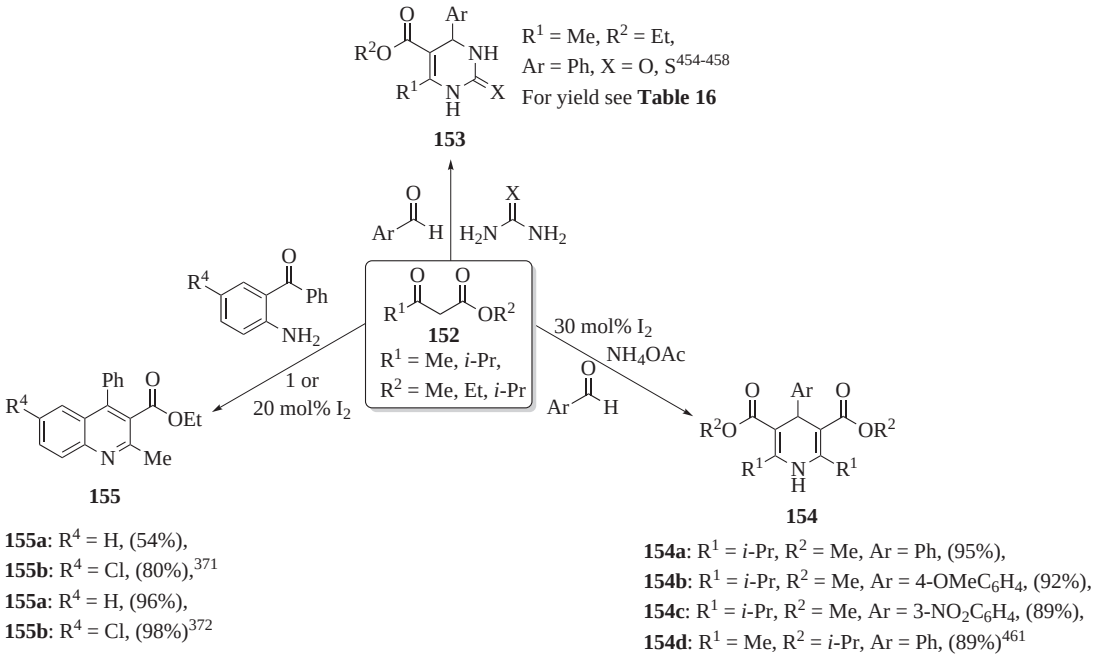
Iodine catalyzed a four-component reaction between ethyl acetoacetate, dimedone, aromatic aldehydes, and NH_4OAc or amines giving 1,4-dihydropyrimidines **154**.[460] Yields were high and independent of the substituents on the aromatic ring of the aldehyde. The solvent of choice was ethanol[461] or methanol,[462] although the reaction also took place under SFRC.[463] Quinolines **155** could be prepared from 1,3-dicarbonyl molecules and 2-aminoaryl ketones under SFRC with a catalytic amount of I_2/SiO_2 within 2.5 h in yields of up to 80% (Scheme 62),[371] or with 1 mol % of iodine in EtOH.[372]

The quinoline skeleton could also be prepared using β-ketoesters or ketones in combination with naphthalene-2-amine and aromatic aldehydes.[302,305–310] β-Ketoesters were also transformed into coumarins[123,124] and into tetrahydro-β-carboline derivatives.[378] **ICT** of β-ketoesters, aromatic amines and aryl aldehydes in MeOH led to the penta- or hexa-substituted piperidines in a single step.[464] Substituted 3-acetylcoumarins underwent one-pot **IC** condensation with substituted 4-amino-5-mercapto-1,2,4-triazoles in DMF under MW irradiation, giving triazolothiadiazines.[465]

Other **IC** cyclization reactions include the transformation of β-ketoesters into β-enaminones[405] or dithioacetals,[277] or the silylation of *p*-nitrobenzyl-2-diazoacetoacetate.[466]

4.3. Anhydrides

Besides the use of Ac_2O as an esterification agent in the protection of carbohydrate hydroxy functionalities,[180,181,183,184] Ac_2O and $(Boc)_2O$[467] were used in **IC** nucleophilic addition-substitution reactions. Aliphatic or aromatic alcohols and phenols were converted into esters **156** in a DCM/$CHCl_3$ solution[63] (Scheme 63) or under SFRC[121] with a fourfold excess of Ac_2O in the presence of 10 mol % of I_2. Transformation was also

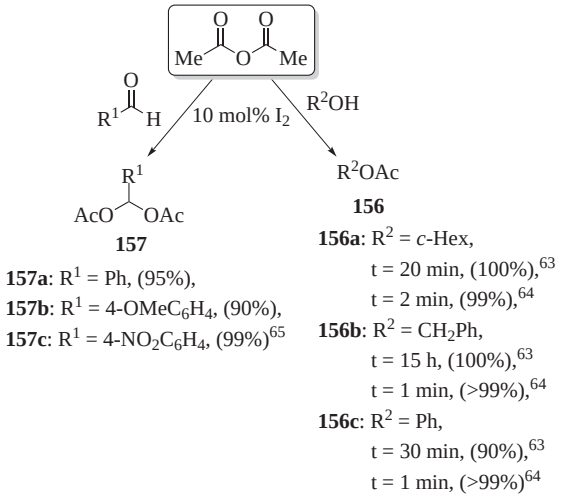


Scheme 62. **IC** cyclizations of β-ketoesters.

Table 16
IC cyclocondensation of ethyl acetoacetate, benzaldehyde and urea (X=O) or thiourea (X=S) to substituted 3,4-dihydropyrimidin-2(1*H*)-ones **153**

Entry	X	Reaction conditions I_2 (mol %)/*T*/solvent/*t*	Yield (%)	Ref.
1	S	39.5/Reflux/MeCN/6.5 h	92	454
2	O	5/Reflux/toluene/4 h	95	455
3	S	10/—[a]/SFRC/1 min	65	456
4	O	10/—[a]/SFRC/1 min	90	456
5	O	10/90 °C/SFRC/20 min	86	457
6	O	40/43–46 °C/MeCN/3 h	73	458

[a] MW, temperature not defined.



Scheme 63. **IC** acetylation of alcohols and aldehydes with Ac_2O.

effectively performed under SFRC; moreover, a stoichiometric amount of Ac_2O was sufficient and the esterification was extremely fast; quantitative yields were achieved in a few minutes.[2,64]

Ac_2O was also reported to react with aromatic, aliphatic and α,β-unsaturated aldehydes to yield the corresponding geminal diacetates **157** in the presence of a catalytic amount of iodine. The nature of the substituents on the aromatic ring had a slight effect on the reaction system. Good water tolerance was observed, since 25% water solution of glutaraldehyde could be transformed into diacylal in 98% yield.[65]

IC acetylation of hemicellulose with Ac_2O afforded a maximum degree of substitution (DS)=1.53 when performed in 1-butyl-3-methylimidazolium chloride,[183] whereas full esterification (DS=3) of starch under MW irradiation took place under SFRC.[184]

5. Transformation of molecules containing sp^2 or sp^3 hybridized oxygen atoms bound to heteroatoms

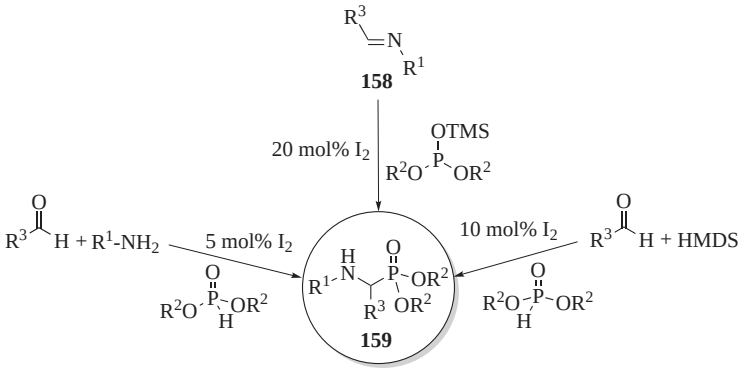
5.1. Phosphonates

Iodine was shown to be a suitable catalyst for the synthesis of phosphonates. Diethyl phosphite in combination with *N*-benzylidene imines **158** furnished α-amino phosphonates **159** (Scheme 64), while aliphatic amines were unsuitable for this reaction. In the case of the three-component reaction in DCM, EDGs on the aniline moiety decreased the yield, while EWGs raised it, and vice versa on the aromatic ring of the aldehyde.[468] Instead of imines, **ICTs** of aryl amine, aryl aldehydes, and diethyl phosphite furnished phosphonates **159**. Reactions worked best in EtOH, and aliphatic aldehydes gave no desired products.[469] An analogous reaction was performed under SFRC and, instead of an aryl amine, HMDS was used. Primary 1-aminophosphonates (**159f** and **159g**) were obtained from aliphatic and aromatic aldehydes and also with ketones in 80–95% yield.[470] The conversion of *N*-tosyl aldimines and dialkyl trimethylsilyl phosphites in the presence of 20 mol % of I_2 in DCM furnished α-sulfonamide phosphonates in high yield.[471] **IC** addition of triethyl phosphite to benzoylhydrazones afforded the corresponding hydrazino-substituted phosphonates in excellent yields of up to 95%.[472]

5.2. Sulfur-containing molecules

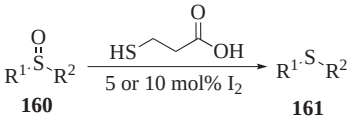
A variety of sulfoxides **160** (Scheme 65) were deoxygenated to sulfides **161** using 3-mercaptopropionic acid in the presence of I_2 in MeCN.

Yields ranged from 55 to 96% for dialkyl, alkyl aryl and diaryl sulfoxides; the lowest yield was obtained in the case of nitrophenyl phenyl sulfoxide.[473] **IC** nucleophilic addition of indoles to *N*-*tert*-butanesulfinyl aldimines resulted in the formation of bis(indolyl) alkanes.[474] An indium/iodine couple triggered an aza-Michael-type



159a: R^1 = Ph, R^2 = Et, R^3 = Ph, (90%),[468]
159b: R^1 = 4-OMeC_6H_4, R^2 = Et, R^3 = Ph, (78%),[468]
159c: R^1 = 4-$NO_2C_6H_4$, R^2 = Et, R^3 = Ph, (93%),[468]
159a: R^1 = Ph, R^2 = Et, R^3 = Ph, (99%),[469]
159b: R^1 = 4-OMeC_6H_4, R^2 = Et, R^3 = Ph, (93%),[469]
159d: R^1 = Ts, R^2 = Me, R^3 = Ph, (93%),[471]
159e: R^1 = Ts, R^2 = Et, R^3 = Ph, (94%),[471]
159f: R^1 = H, R^2 = Et, R^3 = Ph, (93%),[470]
159g: R^1 = H, R^2 = Et, R^3 = *n*-Pr, (85%)[470]

Scheme 64. IC synthesis of phosphonates.



161a: R^1 = R^2 = Bu, (93%),
161a: R^1 = Ph, R^2 = *i*-Pr, (89%),
161b: R^1 = R^2 = Ph, (95%),
161c: R^1 = Ph, R^2 = 4-$NO_2C_6H_4$, (55%)[473]

Scheme 65. IC deoxygenation of sulfoxides.

addition of nitroarenes to vinyl sulfones.[475] Iodine was also shown to successfully catalyze the oxidation of methane in oleum.[476–478] Iodine efficiently catalyzed the synthesis of symmetrical diaryl sulfoxides from thionyl chloride and aromates; nitro-substituted aromatics failed to react.[479]

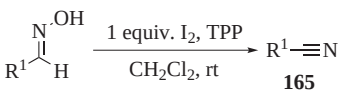
5.3. Boron-containing molecules

Iodine/palladium mediated a modified Suzuki-type coupling of bicyclic hydrazines with organoboronic acids **162** and produced *trans*-3,4-disubstituted hydrazino cyclopentenes **163** upon stereoselective ring opening (Scheme 66).[480,481] Interestingly, **IC** (20%) Suzuki–Miyaura coupling between arylboronic acids and aryl halides to unsymmetrically substituted biaryls **164** was accomplished in an air atmosphere in polyethylene glycol 400 (PEG 400) in the presence of K_2CO_3.

The reaction also worked well with (*E*)-β-bromostyrene and phenylboronic acid; the double-bond stereochemistry was retained.[482] Additionally, homocoupling of arylboronic acids to the corresponding biaryl derivatives **164** promoted with I_2/K_2CO_3 took place in PEG 400 in air. *ortho*-Substituted arylboronic acids gave low or no biaryl product, due to the steric hindrance, in contrast to *para*-substituted substrates that gave good results (Scheme 66).[483]

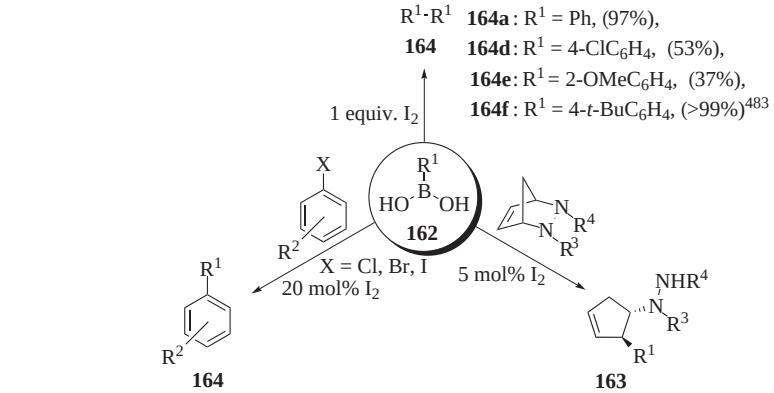
5.4. Oximes

Aliphatic and aromatic oximes reacted with stoichiometric amounts of I_2/PPh_3 (I_2/TPP) in DCM, affording the corresponding nitriles **165** (Scheme 67); substituents had little effect on the reaction rate.[484] Iodine in a stoichiometric amount in MeCN was shown to be an efficient deoximating agent.[485] Deprotection of oximes using a catalytic amount of iodine in aqueous solutions of amphiphilic SDS proceeded under mild conditions at 25–40 °C within 5 h.[486] **IC** regeneration of carbonyl molecules from oximes was achieved with 30% H_2O_2 in aqueous MeCN.[487]



165a: R^1 = Ph, (92%),
165b: R^1 = 4-ClC_6H_4, (93%),
165c: R^1 = 3-pyridyl, (84%),
165d: R^1 = *n*-pentyl, (87%)[484]

Scheme 67. IC synthesis of nitriles from oximes.



164a: R^1 = Ph, (97%),
164d: R^1 = 4-ClC_6H_4, (53%),
164e: R^1 = 2-OMeC_6H_4, (37%),
164f: R^1 = 4-*t*-BuC_6H_4, (>99%)[483]

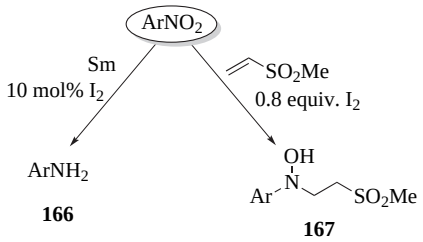
164a: R^1 = Ph, R^2 = H, (75%), (X was I),
164b: R^1 = 4-ClC_6H_4, R^2 = H, (>98%), (X was I),
164c: R^1 = Ph, R^2 = 4-OMe, (84%), (X was I),
164b: R^1 = Ph, R^2 = 4-Cl, (55%), (X was I),
164a: R^1 = Ph, R^2 = H, (73%), (X was Br),
164a: R^1 = Ph, R^2 = H, (28%), (X was Cl)[482]

163a: R^1 = Ph, R^3 = R^4 = COOEt, (93%),
163b: R^1 =  , R^3 + R^4 =  , (61%),
163c: R^1 = Ph, R^3 + R^4 =  , (86%),[480] (35%)[481]

Scheme 66. Transformation of substituted boronic acids in the presence of iodine.

5.5. Nitro compounds

Aromatic nitro compounds were selectively reduced to anilines **166** (Scheme 68) with 4 equiv of samarium in the presence of 10 mol % of I_2. No dehalogenation or hydrogenolysis were observed during the process, although the reduction of ethyl 2-nitrobenzoate yielded methyl 2-aminobenzoate **166b** because of transesterification, since the reaction mixture was refluxed in methanol.[488]



166

167

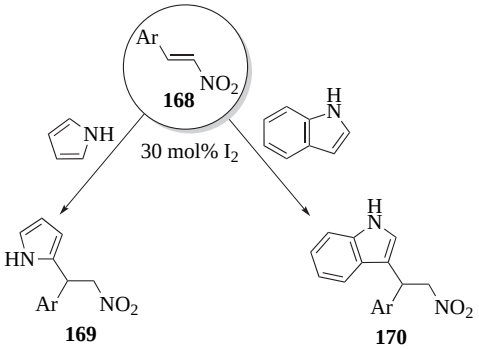
166a: Ar =4-$OMeC_6H_4$, (88%),
166b: Ar =2-$COOMeC_6H_4$, (86%),
166c: Ar =1-pyrenyl, (92%)[488]

167a: Ar =Ph, (77%),
167b: Ar =2-MeC_6H_4, (77%),
167c: Ar =4-FC_6H_4, (78%)[475]

Scheme 68. ICT of nitroaryl compounds.

Similarly, reduction to amines with the Sm/I_2 system can be done in aqueous THF.[489] An I_2/In couple catalyzed the 1,4-addition of nitroarenes to α,β-unsaturated sulfones to produce 2-(*N*-hydroxylamino)sulfones **167**. The reaction proceeded best in MeOH and substituent effects had a minimal influence on the yield.[475]

The above-mentioned reactions resulted in the reduction of the nitro group, whereas the Michael addition of pyrrole or indole to β-nitrostyrenes **168** with 30 mol % I_2 proceeded with preservation of the nitro group, yielding the corresponding adducts **169** and **170**. Electronic effects had no significant influence on the yield, although EDGs on the aromatic ring of the nitrostyrene resulted in longer reaction times (Scheme 69).[490]



169

170

169a: Ar =Ph, (86%),
169b: Ar =4-ClC_6H_4, (76%),
169c: Ar =4-$OMeC_6H_4$, (79%)[490]

170a: Ar =Ph, (99%),
170b: Ar =4-ClC_6H_4, (99%),
170c: Ar =4-$OMeC_6H_4$, (99%)[490]

Scheme 69. IC conjugative addition of heteroaromatics to β-nitrostyrenes.

6. Conclusions

Iodine has been a catalyst of substantial application in recent years; it is a remarkably versatile, flexible and multipurpose catalyst. It is capable of catalyzing the formation and scission of a broad range of different bonds, regardless of the hybridization of the atom. The ever-growing relevance and concern of modern chemistry is for the protection of the environment. Solid-supported iodine with unreduced activity could considerably contribute to green chemistry. There have been only a few reports of solid-supported iodine as a catalyst thus far; this type of catalyst could be of a future perspective in terms of green chemistry and sustainable development. There is an open debate about the nature of the actual catalyst in I_2-catalyzed reactions, particularly when conducted in protic solvents. There are a plethora of papers, but very little mechanistic explanation is given. It is known that iodine in methanol produces HI, although the reaction is not efficient.[491] When a third reactant is present, the electron flow may be productive, if the order of the addition of the reagents is correct.[492] A large majority of the publications have operated with tentative schemes; many have speculated about HI or ROI formation as the driving force. Some mechanistic assumptions were made on the basis of the effects of the added bases. It should be borne in mind that base, besides quenching HI, also reduces the reactivity of iodine. SFRC may reduce this dilemma to some degree, although it is not clear if HI or ROI could be formed from iodine and a molecule bearing a hydroxy or carboxy group. Another possibility might be the complexing of iodine with two or three reactants to a well-organized arrangement, which is responsible for the formation of the products. In favour of this hypothesis could be the iodine-catalyzed acetylation of *exo*- and *endo*-norborneol, furnishing only nonrearranged products.[2,48] Regardless of these facts, the reaction courses are probably not uniform, and much investigation has yet to be undertaken in order to obtain a deeper insight and understanding of the iodine-catalyzed transformation.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.086.

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Biographical sketch

Marjan Jereb obtained his B.Sc. degree and completed his Ph.D. degree at the University of Ljubljana in 2001, under the supervision of Prof. Zupan and Dr. Stavber. In 2004–2005, he spent a year at the ETH Zurich in the group of Prof. Antonio Togni as a postdoctoral associate. He is currently an Assistant Professor at the Faculty of Chemistry and Chemical Technology of the University of Ljubljana. His main research interest is focused on organohalogen chemistry, emphasizing the green chemical approach.

Dejan Vražič studied chemistry at the University of Ljubljana and received his B.Sc. in 2007 under the supervision of Prof. Marko Zupan. In 2008 he joined "Jožef Stefan" Institute, Ljubljana and started his postgraduate study as a Ph.D. student at the Faculty of Chemistry and Chemical Technology at the University of Ljubljana under supervision of Assistant Professor Marjan Jereb and Associate Professor Stojan Stavber. His research interest is halogenation, halogens as mediators of organic transformation and green chemistry.

Marko Zupan received his B.Sc. and M.Sc. degrees from the University of Ljubljana and also obtained his Ph.D. there in 1974. He is a Professor of Organic Chemistry at the Faculty of Chemistry and Chemical Technology of the University of Ljubljana. He is one of the pioneers of modern organohalogen chemistry, which remains his main scientific interest, along with research in the fields of polymer-supported reagents and catalysts, photochemistry of organic compounds and organic green chemistry.