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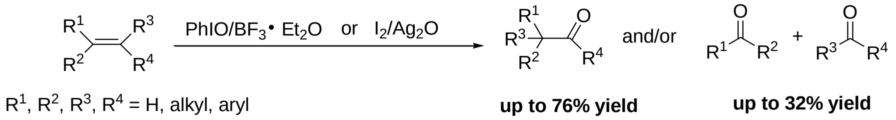
Oxidative cleavage and rearrangement of olefins using iodosylbenzene or iodine

Nizam Havare
Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, Freiburg im Breisgau, Germany

Abstract

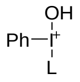


The work is about oxidative rearrangement of olefins using a hypervalent λ3-iodine complex. Aryl and alkyl substituted olefins reacts with iodobenzene bortrifluorid diethyl etherate complex, which is subordinated as the hypervalent λ^3-iodan complexes, to the corresponding aldehyde and/or ketones up to good yields. A mechanism for the rearrangement reaction was proposed.

Keywords: iodine, olefins, oxidative cleavage

Introduction

Hypervalent λ^3-iodan reagents such as iodosyl benzene (PhIO), (diacetoxyiodo)benzene or iodine triacetate react with acids or lewis acids to form hydroxy- λ^3-iodan complexes 1 and allow preparation a broad range of compounds in mild reaction conditions (figure 1) [1]. However, they decompose with different half-lives to give a black tar and/or PhI [2].

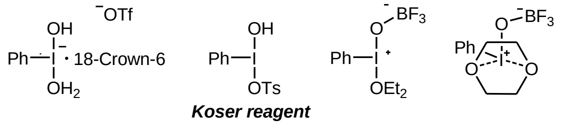


1

L = 18 crown 6, $^-BF_4$, BF_3, OEt_2, ^-OTs, ^-OH, Solvents

Fig 1: Hydroxy-*λ*^{3}-iodan complexes 1

The oxidative cleavage of C=C double bonds to the corresponding carbonyl compounds is one of the traditionally most important reactions in the organic synthesis [5]. Ozonolysis is the generally accepted standard method in both industrial and preparative chemistry for oxidative cleavage to form ketones and/or aldehyde [6]. However, because of the latent explosion, the methode is not useful for a broad range of olefins [7]. Metal oxides in high oxidation states such as RuO_4, OsO_4 or $NaIO_4$ (Jones reagent) are expensive and/or toxic [8a, b]. A better method was presented by Ochiai *et al.* in 2007 for the oxidative cleavage of olefins with the complex 2 in water. However, the method was used only for aryl alkenes [8c].



2 **3** **4a** **4b**

Fig 2: Complex 2 was used for the oxidative cleavage of olefins [8c]

The oxidative rearrangement of olefins react with following reagents: mercury sulphate [9a], mercuric nitrate [9b], Thallium (III) nitrate [10], $K_2S_2O_8/CuSO_4$ [11], 2,4,6-triphenylpyrylium tetrafluoroborate [12], I_2/HgO [13], I_2/Ag_2O [14] and metal (porphyrin) reagents such as Oxochromium(V)porphyrin [15], Fe (III) (tetraphenylporphyrin)/PhIO [16], Mn (III)(mesotetrakis (2,6-dichloro-phenyl) porphyrin/*m*-CPBA [17], hypervalent iodine reagents such as PhIO/BF_3 Et_2O [18], PhIO/H_2SO_4 [19], $PhI(OAc)_2$ /H_2SO_4 [20] or $PhI(OAc)_2/NaHSO_4$ H_2O [21] to form the corresponding aldehydes and/or ketones. Koser *et al.* [22] could synthesize a new hydroxy-λ^3-iodan complex, called "*Koser reagent*" 3: hydroxy(tosyloxy)iodo] benzene (HTIB). They found that aromatic olefins rearrange using HTIB in moderate yield to the corresponding ketones. An alternative method for the oxidative rearrangement of aromatic olefins has been reported using PhIO/BF_3 Et_2O also. However, this procedure was only applied to *cis*- Stilbenes and cyclohexene [18].

Results and Discussion

I tested here the oxidative cleavage and/or rearrangement of some of alkyl and aryl alkenes using complex 4a, which is prepared in *situ*. I tested first the rearrangement of *cis*-stilbene using complex 4a to optimize the reaction condition (table 1). If the reagent PhIO/BF_3 Et_2O carried out with 18-crown-6 is used, there is no reaction after a day (entry 1). If the reaction carried out in dichloromethane, there are no specific isolable products (entry 2). In the presence of 1,4-dioxane was moderate yield obtained (entries 3,4). The different mix of dichloromethane and 1,4-dioxane improved the reactivities and yields (entries 7-11). The best yield was obtained by mixing of dichloromethane and 1,4-dioxane (20:1) (entry 11) [23].

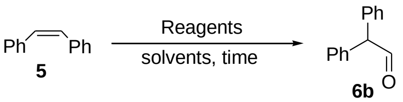


Table 1: Optimization of the reaction condition.

Entry	Reagents in presence of Molsieve 4Å	Solvents	Temp.	Time	Conversion (%)^b	yield (%)
1	PhIO/BF_3·Et_2O / 18-crown-6	CH_2Cl_2	0°C→RT	24 h	no reaction	
2	PhIO/BF_3·Et_2O	CH_2Cl_2	r.t.	5 min.	87	3
3	PhIO/BF_3·Et_2O	1,4-Dioxane	r.t.	5 min.	14	12
4	PhIO/BF_3·Et_2O	1,4-Dioxane	r.t.	80 min.	33	23
6	PhIO/BF_3·Et_2O	1,4-Dioxane	r.t.	2 h	35	30
7	PhIO/BF_3·Et_2O	CH_2Cl_2/1,4-Dioxane (1:1)	r.t.	10 min.	41	33
8	PhIO/BF_3·Et_2O	CH_2Cl_2/1,4-Dioxane (5:1)	r.t.	10 min.	47	46
9	PhIO/BF_3·Et_2O	CH_2Cl_2/1,4-Dioxane (100:1)	r.t.	5 min.	74	46
10	PhIO/BF_3·Et_2O	CH_2Cl_2/1,4-Dioxane (20:1)	r.t.	10 min.	63	54
11	PhIO/BF_3·Et_2O	CH_2Cl_2/1,4-Dioxane (20:1)	r.t.	5 min.	54	54

I tested nine substrates that gave up to good yields in the rearrangement and oxidative cleavage in both reaction pathways (table 2). I obtained a black tar by long stirring of reaction mixture in these reaction conditions. Why the difference between conversion and isolated yields so big is, is unclear. I assume that the the acidity of the used acid and/or the use of solvent play a key role to obtain a high yield. The half-live of the *insitu* formed complex 4a play also role. It is well known that the half-live of the λ^3-iodan-complexes strongly depend on the acidity of the used acid [8c]. The reactions in table 2 should be optimized using soft acids or lewis acids. 1-phenylcyclohexene 7a reacts with complex 4a to give a rearrangement product 7c and a ketone 7b in low yield (entry 1, table 2). Cyclohexene rearranges to cyclopentanecarbaldehyde in 1,4-dioxane (entry 2, table 2). However, the rearrangement reaction of cycloheptene occurs in traces (entry 4, table 2). In 1,4-dioxane reduce cycloheptene to 1,3-cycloheptandiene (entry 3, table 1). The oxidative rearrangement of cycloheptene proceeds in 1,4-dioxane very low yield (entry 5, table 2). A better yield for the rearrangement was obtained using iodine and silver oxide, which was with this reagent have not been tested before (entry 5, table 2). Cycloheptanone was also obtained as a side product (entry 5, table 2). *cis*-Cyclooctene rearrange to cycloheptcarbaldehyde using iodine and silver oxide in moderate yield, and oxidize to cyclooctanone in low yield (entry 6, table 2). However, if complex 4a was used as a reagent, *cis*-cyclooctane react to *cis*- and *trans*-1,3-cyclooctadiene in very low yield (entry 7, table 2). Styrene oxidizes and/or rearrange also to phenylacetaldehyde in a modarate yield. I could show in our previous work that epoxides such as *β*,*β*-d2-styrene oxide rearrange and cleavage in 2:1 ratio (rearrangement product: oxidative cleavage product) [2]. An experiment with *β*,*β*-d2-styrene can provide information about the ratio of rearrangement product compared to oxidative cleavage product (entry 8, table 2). Both the rearrangement reaction of 1,2-dihydronaphthalene (entry 9, table 2) and benzosuberene proceeds (entry 10, table 2) in low yields. The conversion of the rearrangement reaction of Benzosuberene to product after long stirring time constant and low (entry 10, table 2). Yield and conversion of the rearrangement reaction of Benzosuberene also doesn`t change, if the temperature of the reaction mixture increases. *trans*-*p*-Chlorostilbene react with complex 4 to give a oxidative cleavage product in a moderate yield (entry 11, table 2). Here, I didn´t observed any rearrangement product. The oxidative rearrangement of *trans*-stilbene was like *cis*-stilbene were also investigated under a wide variety of reaction conditions (entries 12-15, table 2). The yield of diphenylacetaldehyde as rearrangement product is in dichloromethane very low (entry 12, table 2). The best yield was obtained in 1,4-dioxane at 0°C and warming slowly to room temperature (entry 15, table 2).

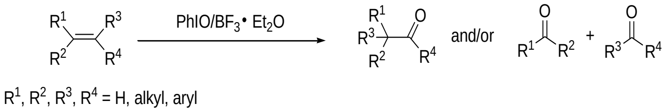
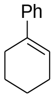
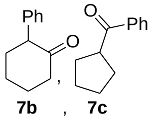
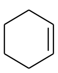
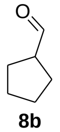
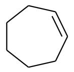
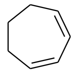
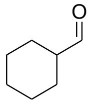
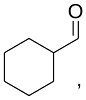
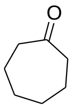
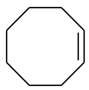
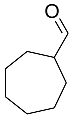
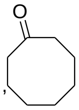
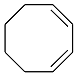
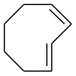
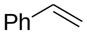
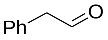
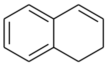
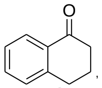
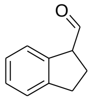
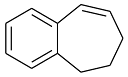
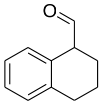
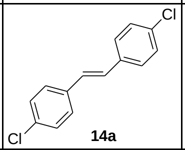
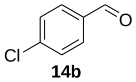
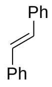
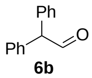


Table 2: ^{a}The yields und conversion were determined by isolation of the products. ^{b}The product was isolated as 1-(Cyclopentylmethylen)-2-(2,4-dinitrophenyl)hydrazine. ^{c}The conversion was not determined. ^{d}The yields and the conversion was determined by addition of internal (*n*-heptane) on achiral GC.^{e}Better yield was obtained using the same reagent at -15°C.^{24} ^{f}The yield and the conversion was determined by GC analysis by addition of internal standard (1,4-dichlorobenzene).

Entry^{a-d}	Substrate	Reagent(s)	Solvent(s)	Temp.	Time	Product(s)	Conver. (%)	Yield (%)
1^a	 **7a**	PhIO/BF_3·Et_2O	CH_2Cl_2	0°C→r.t.	2 day	 **7b** , **7c**	83	19,12
2^{b,c,e}	 **8a**	PhIO/BF_3·Et_2O/ molsieve 4Å	1,4-dioxane	0°C→r.t.	3.5 h	 **8b**	-^{c}	29

3^{d}	 **9a**	PhIO/BF$_3$·Et$_2$O/ molsieve 4Å	1,4-dioxane	r.t.	3 day	 **9b**	30	14
4		PhIO/BF$_3$·Et$_2$O/ molsieve 4Å	1,4-dioxane/CH$_2$Cl$_2$ (4:1)	r.t.	4 day	 **9c**	4	4
5^{f}		I$_2$/Ag$_2$O	1,4-dioxane	r.t.	13 day	 ,  **9c** , **9d**	100	76 (**9c**) ,21 (**9d**)
6	 **10a**	I$_2$/Ag$_2$O	CH$_2$Cl$_2$	r.t.	16h	 ,  **10b** **10c**	96	37 (**10b**), 13 (**10c**)
7		PhIO/ BF$_3$·Et$_2$O/ Molsieb 4Å	CH$_2$Cl$_2$	r.t.	2 h	 ,  **10d** **10e**	74	9 (**10d**) 7 (**10e**)
8^{a}	 **11a**	PhIO/BF$_3$·Et$_2$O	1,4-Dioxan	r.t.	2 h	 **11b**	90	41
9^{d}	 **12a**	PhIO/BF$_3$·Et$_2$O/ Molsieve 4Å	CH$_2$Cl$_2$	0°C→r.t	34 min.	 , **12b**  **12c**	94	21, 17
10^{a}	 **13a**	PhIO/BF$_3$·Et$_2$O	1,4-dioxane	r.t.	1 day	 **13b**	12	12
11^{a}	 **14a**	PhIO/BF$_3$·Et$_2$O	1,4-dioxane	r.t.	4.5 h	 **14b**	70	32
12	 **6a**	PhIO/ BF$_3$·Et$_2$O/ molsieve 4Å	1,4-dioxane	r.t.	1 day	No reaction		
13^{d}		PhIO/ BF$_3$·Et$_2$O/ molsieve 4Å	CH$_2$Cl$_2$	r.t.	5 min.	 **6b**	84	11
14^{d}			CH$_2$Cl$_2$ /1,4-dioxane (1:4)	r.t.	5 min.		75	22
15^{d}			1,4-dioxane	r.t.	5 min.		30	30
16^{d}			1,4-dioxane	0°C→r.t	4 h		44	38

I assume that the oxidative rearrangement reaction of olefins proceeds as follows; λ^3-iodan-complex 4a forms first of all in *situ*. In the presence of 1,4-dioxane could also form complex 4b (figure 2) Olefin can attack now to the electrophilic complex and results in intermediate 15 by separation of diethyl ether. It allows forming the carbocation and the rearrangement of the potential groups (R^3 or R^4) to carbocation in the absence of water to form intermediate 16. By oxidative cleavage of iodobenzene and BF$_3$·Et$_2$O result the product 17. Another possible reaction pathway is, after olefin attack as a nucleophile to the complex 4 forms the first intermediate 19 bearing a carbocation, which is eliminated a α-proton to form an intermediate 20. After the second elimination of the proton form the corresponding product 21 (Fig 3).

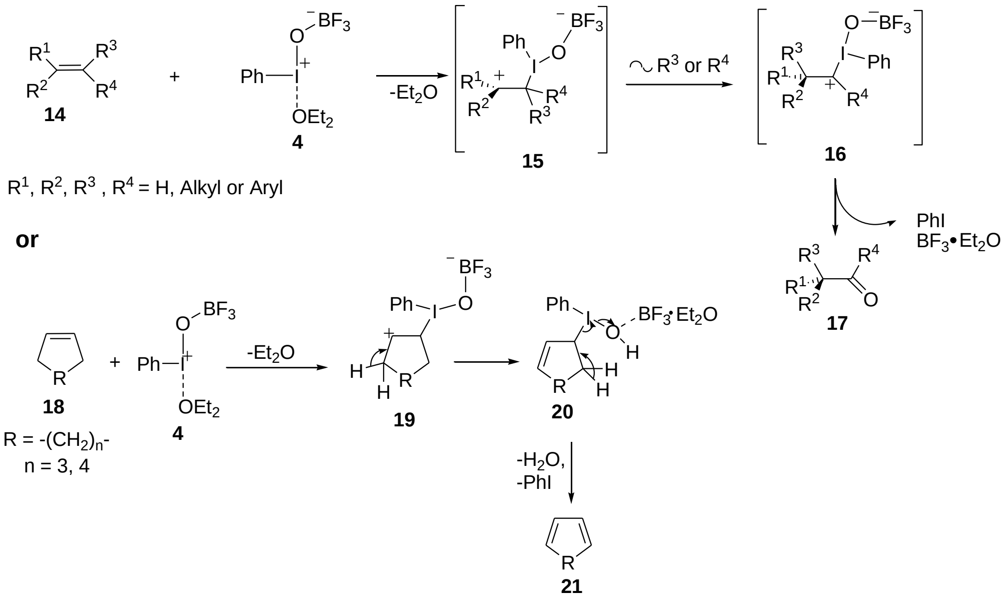


Fig 3: Proposed reaction mechanism

Conclusion

I developed a method for the synthesis of alkyl- and/or arylcarbaldehyds up to moderate yields starting from olefins using iodosylbenzene and bortrifluoriddiethyletherate as lewis acids. A mechanism was suggested for the rearrangement reaction.

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