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Oxidative Opening of Cycloalkanols: An Efficient Entry to ω-Iodocarbonyl Compounds**

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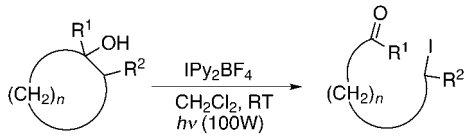
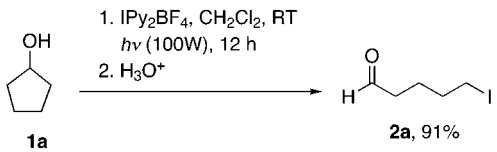
The development of new approaches to elaborate the carbon backbone of organic compounds is among the central issues in organic synthesis. In this regard, a general method for the direct conversion of readily available cyclic alcohols to bifunctional derivatives, such as ω-iodocarbonyl compounds, is an attractive synthetic goal.[1] Herein, we report on a powerful method for synthesizing iodinated derivatives of both, aldehydes and ketones.[2] Thus, bis(pyridine)iodonium(I) tetrafluoroborate (IPy_2BF_4)[3] promotes a regioselective opening reaction of **1** upon irradiation leading to compounds **2** (Scheme 1).[4]



1 **2**

Scheme 1. IPy_2BF_4-promoted regioselective opening of cycloalkanols. R^1, R^2: H, CH_3; n: 2, 3, 4, 10; nine examples (76 – 94 %).

In preliminary studies, cyclopentanol (**1a**) was recovered unreacted upon treatment with IPy_2BF_4. Moreover, NMR experiments revealed that in the absence of visible light no change had taken place even after several days at room temperature. Interestingly, when the mixture was photoactivated (irradiation, 100 W lamp) a clean transformation took place affording 5-iodopentanal (**2a**)[5] in excellent yield after hydrolysis [Eq. (1)].



1a **2a**, 91% (1)

This is an elusive transformation for a secondary alcohol, only accomplished previously for cyclopentanol derivatives.[6] Our method offers a more efficient entry to achieve this scission reaction even from **1a**.[7] This stimulated us to further investigate its scope and convenience, in search for a clean

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and general strategy to produce aldehydes from this rearrangement.[8] It also provided an opportunity to explore the behavior of the iodinating reagent IPy_2BF_4 under this new type of activation; thus, expanding the application profile already established for IPy_2BF_4 in electrophilic chemistry.[3]

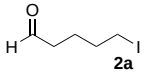
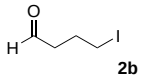
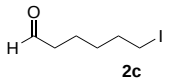
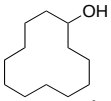
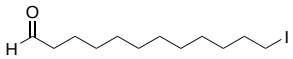
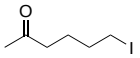
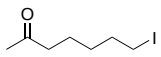
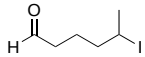
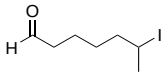
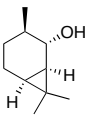
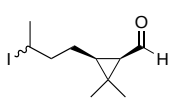
The photolytic reactions were conducted using 2 mmol of the starting cycloalkanol, typically dissolved in CH_2Cl_2 (20 mL), unless otherwise specified (see Table 1). Under photoactivation conditions, ring-opening of cyclobutanol (**1b**) by reaction with IPy_2BF_4 was successful, furnishing **2b**[9] in 92% yield, as sole reaction product (Table 1, entry 2). Cyclohexanol (**1c**) was found to undergo a sluggish reaction in which a significant amount of cyclohexanone (**3**) was formed as by-product. The opening of **1c** required excess of the iodonium source, but even in this case, a considerable amount of unreacted starting material was recovered.

Alkoxyl radicals are widely accepted as intermediates in β-scission processes.[10] Thus, upon activation of the substrate by the iodinating reagent, a base might assist the process by removing hydrogen. This deprotonation might be crucial to drive the process when the ring-opening of the corresponding cycloalkanol is not a particularly favored reaction.

In agreement with this, the reaction of **1c** went to completion by using an excess of cesium carbonate (Table 1, entry 3, Scheme 2a).

We were interested in comparing this approach to **2c** with that based on the reaction of $PhI(OAc)_2/I_2$ with cyclohexanol, which has not been reported to date. When the reaction was performed in cyclohexane as solvent,[11] the β-scission product **2c** was obtained in 20% yield from a mixture that contains cyclohexanone (**3**) (21%), iodocyclohexane as the major reaction product, as well as the expected iodobenzene (Scheme 2b). The experiment results in a noteworthy C–H activation of the alkane used as solvent,[12] but it reveals limitations for the opening of cyclohexanol, subject of comparison. We also tested the reaction using CH_2Cl_2 as solvent,[2b] in this case **2c** was isolated in better yield (45%; Scheme 2c); however, the formation of two new by-products (**4** and **5**) was also observed, arising from the evolution of **2c** in the reaction media. A slight improvement of the process was accomplished by increasing the amount of oxidant system to achieve full conversion of **1c**. Under these conditions, **2c** was obtained in 62% yield but significant overoxidation to **4** and **5** took place (Scheme 2d).

Table 1. Synthesis of ω-iodocarbonyl compounds **2** from cycloalkanols **1**.

Entry	Substrate **1**	IPy_2BF_4 [equiv]	Cs_2CO_3 [equiv]	Product **2**	Reaction time [h]	Yield[a] [%]
1	 **1a**	1.25	–	 **2a**	12	91
2	 **1b**	1.25	–	 **2b**	12	92
3	 **1c**	2.5	10	 **2c**	20	85[b]
4	 **1d**	2.5	10	 **2d**	20	76[b]
5	 **1e**	1.25	5	 **2e**	8	93
6	 **1f**	1.25	5	 **2f**	8	88
7	 (+)-**1g**	1.25	–	 **2g**	12	92
8	 (+)-**1h**	1.25	5	 **2h**	14	89
9	 (–)-**1i**	1.25	5	 **2i**	7	94

[a] Yield of **2** based on starting cycloalkanol **1**. [b] A 0.02 M solution of the alcohol was used.

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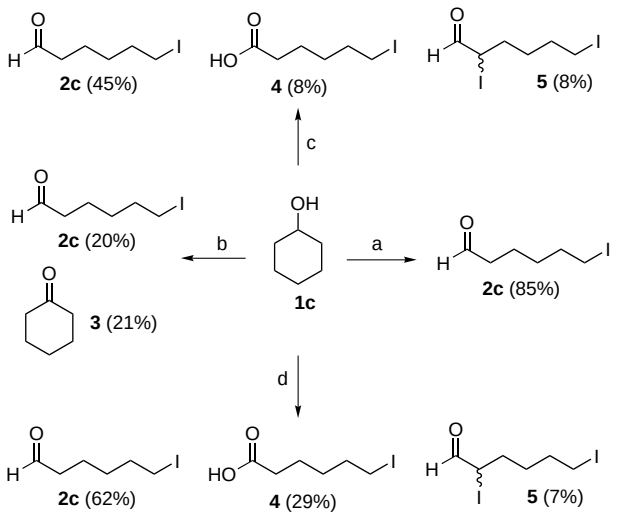


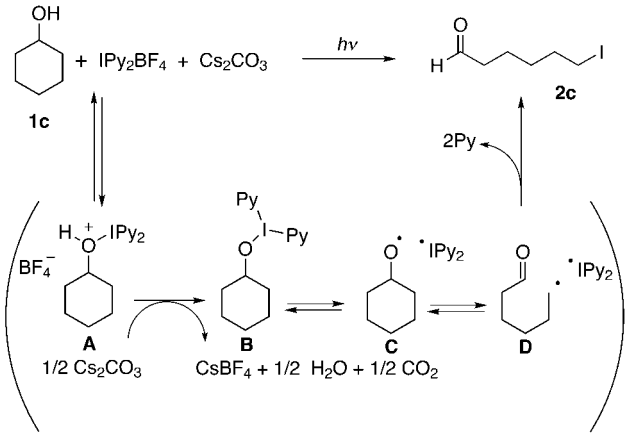
Scheme 2. Approaches for the conversion of cyclohexanol (**1c**) to 6-iodohexanal (**2c**). a) 1. IPy_2BF_4 (2.5 equiv), Cs_2CO_3 (10 equiv), CH_2Cl_2, RT, *hν* (100 W), 20 h; 2. H_3O^+; b) $PhI(OAc)_2/I_2$ (1.1/ 1 equiv), cyclohexane, RT, *hν* (2 × 100 W), 3 h; c) $PhI(OAc)_2/I_2$ (1.1/ 1 equiv), CH_2Cl_2, RT, *hν* (2 × 100 W), 4 h; d) $PhI(OAc)_2/I_2$ (2.2/2 equiv), CH_2Cl_2, RT, *hν* (2 × 100 W), 4 h.

The efficiency of IPy_2BF_4 to promote the conversion of cycloalkanols to iodocarbonyl compounds was also tested on larger ring-size cycloalkanols, such as **1d**. This process opens a new entry to long-chain *ω*-bifunctional compounds, such as **2d** (Table 1, entry 4). Moreover, entries 5 and 6 in Table 1 show that tertiary cycloalkanols **1e** and **1f** can be smoothly ring-opened to furnish iodoketones,[2] proving the generality of the methodology.

Another interesting feature was observed in reactions of racemic **1g** or **1h** which, upon treatment with IPy_2BF_4, afforded only one regioisomer of pure aldehydes **2g** and **2h**, respectively, in excellent yield[13] (Table 1, entries 7 and 8). The preparation of **2h** required cesium carbonate to accomplish total conversion of the alcohol. The opening of the terpene derivative **1i**[14] gives a remarkable example of the efficiency and regioselectivity offered by the IPy_2BF_4/Cs_2CO_3 system to generate aldehydes featuring remote iodine functionality (Table 1, entry 9). Again, the structure of the substrate exerts full control over which C–C bond is cleaved. This leads to the interesting cyclopropanecarbaldehyde framework of **2i**, as 1:1 mixture of diastereoisomers with respect to the newly formed stereocenter.[15]

In terms of reaction mechanism, this process could involve the generation of different reactive species in a sequential manner, as depicted in Scheme 3.[16] Thus, upon mixing the reagents, **1c** would give the oxonium ion **A** and Cs_2CO_3 might promote its evolution to the λ^3-iodane **B**. The key alkoxyl radical **C**, obtained by photolytic homolysis of **B**,[10, 17] could undergo a well documented *β*-scission reaction to afford **D**.[18] Finally, radical capture by the λ^3-iodanyl radical would lead to **2c**. This mechanism would account for the formation of a mixture of diastereomers from **2i** as well as for the observed regioselectivity.[19]

In summary, a mild and efficient process is reported to smoothly conduct the conversion of representative cyclic



Scheme 3. Proposed reaction mechanism for the conversion of cycloalkanols **1** to the iodocarbonyl compounds **2** by means of IPy_2BF_4.

alcohols to useful *ω*-iodocarbonyl derivatives under environmentally friendly and practicable conditions, using simple commercial reagents and visible light. Further studies on the reactivity of IPy_2BF_4 with alcohols are in progress.

Experimental Section

All reactions were carried out under a positive pressure of nitrogen. Dichloromethane was dried by refluxing over CaH_2 and distilled under a nitrogen atmosphere.

Synthesis of **2f**: Cs_2CO_3 (3.72 g, 10 mmol, 5 equiv) was added to a well stirred solution of IPy_2BF_4 (930 mg, 2.5 mmol, 1.25 equiv) in dry CH_2Cl_2 (20 mL) at room temperature. Then, **1f** (228 mg, 2.0 mmol, 1.0 equiv) was added, and the mixture was irradiated (100 W) for 8 h. The mixture was then cooled in an ice–water bath and then quenched with 1M H_2SO_4 (50 mL). The mixture was extracted by using CH_2Cl_2 (4 × 20 mL), and the combined organic layers were washed with sodium thiosulfate (5% solution in water, 2 × 30 mL) and water (2 × 30 mL), and dried over sodium sulfate. The solvent was removed at reduced pressure. The resultant oil was further purified by column chromatography (hexane/ethyl acetate 10/1) yielding **2f** as a pale-yellow oil (422 mg, 88%). Representative data for **2f**, IR (neat): $\tilde{\nu}$: 1714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.12$ (t, $J =$ 6.9 Hz, 2H), 2.39 (t, $J = 7.2$ Hz, 2H), 2.07 (s, 3H), 1.76 (q, $J = 6.9$ Hz, 2H), 1.5–1.1 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.3$, 43.1, 32.9, 29.7 (×2), 22.3, 6.5; elemental analysis (%) calcd for $C_7H_{13}IO$: C 35.02, H 5.45; found: C 35.17, H 5.31.

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[1] This is in sharp contrast to the existence of many synthetic alternatives to conduct the reverse process, namely the reductive ring-closing reaction of *ω*-iodocarbonyl compounds by metal-based Barbier-type approaches and radical cyclization reactions.

[2] The existing methodology is suitable only for the synthesis of ketones from tertiary cycloalkanols. For this purpose, the $PhI(OAc)_2/I_2$ system, known as Suárez's reagent, has been used, mainly for compounds featuring well defined stereoelectronic requirements; for representative examples, see: a) P. Wipf, D. A. Mareska, *Tetrahedron Lett.* **2000**, *41*, 4723–4727; b) R. Hernández, E. I. León, P. Moreno, E. Suárez, *J. Org. Chem.* **1997**, *62*, 8974–8975; c) A. Boto, C. Betancor, E. Suárez, *Tetrahedron Lett.* **1994**, *35*, 5509–5512; d) C. W. Elwood, G. Pattenden, *Tetrahedron Lett.* **1991**, *32*, 1591–1594; for the use of HgO/I_2 see: e) S. Bond, P. Perlmutter, *Chem. Commun.* **2000**, 567–568; f) H. Suginome, S. Yamada, *Tetrahedron Lett.* **1987**, *28*, 3963–3966.

[3] IPy_2BF_4 is a commercial reagent available from either Novabiochem or Aldrich. For a brief overall review of early applications, see: J. Barluenga, *Pure Appl. Chem.* **1999**, *71*, 431–436.

[4] All compounds **2** were characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis and/or high-resolution mass spectrometry data.

[5] Overall, it represents a formal and selective remote activation of aldehydes under mild conditions. For alternative syntheses from a bifuntional system, see: a) C. F. Sturino, A. G. Fallis, *J. Am. Chem. Soc.* **1994**, *116*, 7447 – 7448; b) G. D. Cuny, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 2066 – 2068.

[6] There are scant reports on this transformation. HgO/I_2 leads to related chemistry in steroids; however, it is not efficient on simple secondary cycloalkanols, see: a) H. Suginome, S. Yamada, *J. Org. Chem.* **1984**, *49*, 3753 – 3762; b) H. Suginome, H. Senboku, *Tetrahedron* **1994**, *50*, 13101 – 13112; c) M. Akhtar, D. H. R. Barton, *J. Am. Chem. Soc.* **1964**, *86*, 1528 – 1536; *N*-iodosuccinimide (NIS) gave poor results in this chemistry: d) T. R. Beebe, A. L. Lin, R. D. Miller, *J. Org. Chem.* **1974**, *39*, 722 – 724; for sparse reports on the application of the PhI(OAc)$_2$/I_2 system to promote the opening of cyclopentanol derivatives see: e) U. P. Spitz, P. E. Eaton, *Angew. Chem.* **1994**, *106*, 2263 – 2265; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2220 – 2222; f) J. L. Courtneidge, *Tetrahedron Lett.* **1992**, *33*, 3053 – 3056.

[7] The process is efficient not only in terms of the yield of the iodo derivative with respect to the starting cycloalkanol but also in terms of the number of iodine atoms required to incorporate just one in the final product and the ease of the isolation step.

[8] For skeletal reorganizations based on C–C bond-breaking reactions see: a) P. M. Wovkulich in *Comprehensive Organic Synthesis*, *Vol. 1* (Eds.: B. M. Trost, I. Fleming, S. L. Schreiber), Pergamon, Oxford, **1991**, pp. 843 – 899; b) P. Weyerstahl, H. Marschall in *Comprehensive Organic Synthesis*, *Vol. 6* (Eds.: B. M. Trost, I. Fleming, E. Winterfeldt), Pergamon, Oxford, **1991**, pp. 1041 – 1070.

[9] 4-Iodobutanal (**2b**) is a key compound in the synthesis of 2-pyrrolinodoxorubicin (an anthracycline antibiotic): A. Nagy, P. Armatis, A. V. Schally, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 2464 – 2469.

[10] a) D. P. Curran in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, pp. 812 – 814 and 817; b) P. Gray, A. Williams, *Chem. Rev.* **1959**, *59*, 239 – 328.

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[12] This C–H activation product is also formed in absence of cyclohexanol. The extension of this observation to related alkanes is being currently analyzed. For related intramolecular C–H activation using this reagent, see reference [6e] and H. Togo, T. Muraki, Y. Hoshina, K. Yamaguchi, M. Yokoyama, *J. Chem. Soc. Perkin Trans. 1* **1997**, 787 – 793; R. L. Dorta, A. Martín, E. Suárez, T. Prangé, *Tetrahedron: Asymmetry* **1996**, *7*, 1907 – 1910; A. F. Barrero, J. E. Oltra, A. Barragán, *Tetrahedron Lett.* **1995**, *36*, 311 – 314; K. Furuta, T. Nagata, H. Yamamoto, *Tetrahedron Lett.* **1988**, *29*, 2215 – 2218.

[13] By GC-MS and NMR analysis of crude reaction mixtures.

[14] Prepared from (–)-2-carene according to H. C. Brown, J. V. N. Vara-Prasad, M. Zaislewicz, *J. Org. Chem.* **1988**, *53*, 2911 – 2916.

[15] An epimerization reaction of the hydrogen at the α-position to the carbonyl group was ruled out by a 2D-NOESY experiment. An intense cross peak for the cyclopropyl hydrogen atoms is observed, which confirms the *cis* relationship between them, as in the starting material **1i**.

[16] We thank the referees for suggestions and in particular to one of them for drawing our attention to the mechanism proposed in Scheme 3.

[17] For recent evidence on the participation of these intermediates in related transformations, see: a) J. Madsen, C. Viuf, M. Bols, *Chem. Eur. J.* **2000**, *6*, 1140 – 1146; b) J. L. Courtneidge, J. Lusztyk, D. Pagé, *Tetrahedron Lett.* **1994**, *35*, 1003 – 1006.

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Chromium – Copper Exchange of Fischer Carbene Complexes: X-Ray Crystal Structure of a [Cu{=CR^1(OR^2)}(MeCN)(Et$_2$O)][PF$_6$] Complex**

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Over the last two decades Fischer-type carbene complexes have become valuable tools in stoichiometric transition metal mediated organic synthesis.[1] The carbene nature of these complexes is demonstrated by their ability to transfer the carbene ligand not only to alkenes (cyclopropanation),[2] but also to oxygen, nitrogen, and carbon through the corresponding ylides (amine oxides and dimethyl sulfoxide; sulfilimines; P–C, S–C, and N_2–C ylides).[3] Although transmetalation is probably the most important single process in organometallic chemistry, particularly for transition metal catalyzed reactions,[4] the simple transfer of a carbene ligand from a metal – carbene complex to another metallic center is rare.[5] Carbene complexes of Rh, Pd, Pt, Cu, and Ag have been formed by transfer of diaminocarbene ligands (imidazolinylidene or imidazolidinylidene ligands, which are found to be readily transferred between metal centers) from Group 6 metal carbene complexes.[5–7] However, the transfer of alkoxycarbene ligands has been reported only for [Mo{=CPh(OMe)}(CO)(Cp)(NO)] to [Fe(CO)$_5$][8] and [W{=CPh(OMe)}(CO)$_5$] to H[AuCl$_4$].[9] Very recently Sierra et al. have proposed palladium biscarbene complexes as the active intermediates in the palladium-catalyzed dimerization of alkoxycarbene – chromium complexes.[10, 11]

In the context of our studies on copper-catalyzed coupling reactions of Fischer carbene complexes we report here on 1) the cross-coupling of Fischer chromium – carbene complexes with ethyl diazoacetate (EDA), and 2) the isolation and full characterization of the first alkoxycarbene complex of copper(I). A recent, excellent report by Hofmann and Straub[12] on the characterization of an alkoxycarbonylcarbene – copper complex has prompted us to release our results.

When chromium – carbene complexes **1** were treated with EDA (2.5 equiv) and CuBr (15 % mol) in THF at room temperature the alkenes **2** were isolated with high yields (80 – 95 %) along with ethyl maleate and ethyl fumarate

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