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Activation of Alkanes upon Reaction with $PhI(OAc)_2 - I_2$**

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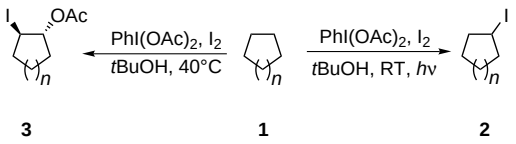
Carbon – hydrogen-bond-activation reactions are challenging processes in organic synthesis.[1] Halogenation reactions have been thoroughly studied and widely practiced and provide a simple and classic way to functionalize hydrocarbons.[2] However, the iodination of alkanes has been a particularly elusive reaction and still remains as an active research area.[3] The endothermic nature of the overall process has been invoked to explain the failure of a radical-chain approach to accomplish this reaction.[4, 5] While performing β-scission reactions of cycloalkanols,[6] we noticed that (diacetoxyiodo)benzene [$PhI(OAc)_2$][7] gave rise to a mixture of compounds, where iodocyclohexane (**2b**) was found as the major product, resulting from an activation of the cyclohexane used as solvent.

Herein we report new approaches to selectively produce either iodoalkanes **2** or 1-acetoxy-2-iodocycloalkanes **3** from readily available hydrocarbons **1**. The products **2** and **3** arise from single and double formal C–H-bond-activation reactions, respectively. This unique reaction manifold can be tuned by treating alkanes **1** with $PhI(OAc)_2$, iodine (I_2), and *tert*-butylalcohol (*t*BuOH) simply by using photochemical or thermal conditions (Scheme 1).

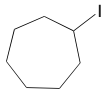
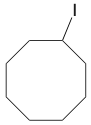
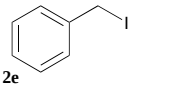
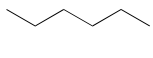
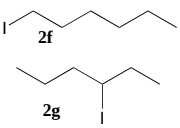
Our initial studies with cyclohexane (**1b**) showed that the presence of an alcohol is necessary for an efficient alkane activation. *t*BuOH was found to be the most effective of all the alkanols tested. Thus, cycloalkanes were cleanly converted into the corresponding iodinated derivatives, under irradiation conditions (2×100 W lamps), in high yield, under relatively mild conditions, and in rather short reaction times. In addition, toluene (**1e**) also gives benzyliodide (**2e**) as the sole reaction product.[8] Linear alkanes react affording mixtures of monoiodinated derivatives in good combined yield, showing high selectivity for secondary positions (Table 1).



Scheme 1. Photochemical and thermal reactivity of hydrocarbons with $PhI(OAc)_2 - I_2$.

An outstanding feature of this iodine(III)-induced activation of alkanes was observed when carrying out the reactions under thermal instead of photochemical conditions.[9] In this case, bifunctional compounds **3** were obtained as major, or even single, reaction products (Scheme 1, Table 2). The global

Table 1. Synthesis of iodoalkanes **2** from alkanes **1**.[a]

Entry	Alkane (**1**)	Concentration [M][b]	Reaction time [h]	Product (**2**)	Yield [%][c]
1	 **1a**	0.04	1.5	 **2a**	98
2	 **1b**	0.04	4	 **2b**	97
3	 **1c**	0.02	6	 **2c**	92
4	 **1d**	0.02	8	 **2d**	85[d]
5	 **1e**	0.02	1	 **2e**	92[e]
6	 **1f**	0.04	4	 **2f**, **2g**, **2h**	85[f]

[a] All reactions performed with the following stoichiometry: $PhI(OAc)_2$ (1 equiv), I_2 (1.1 equiv), *t*BuOH (1 equiv). The alkane was used as solvent. [b] Referred to iodine. [c] GC yield unless otherwise specified. [d] Compound **2d** was isolated in 80 % yield upon column chromatography with *n*-hexane as eluant. [e] Determined by ^{1}H NMR spectroscopy. [f] Proportions of isomers (determined by GC): **2g**:**2h** = 1:1.5, **2f**:**2g** + **2h** = 1:15.

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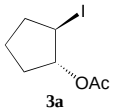
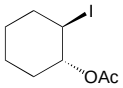
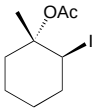
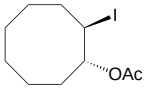
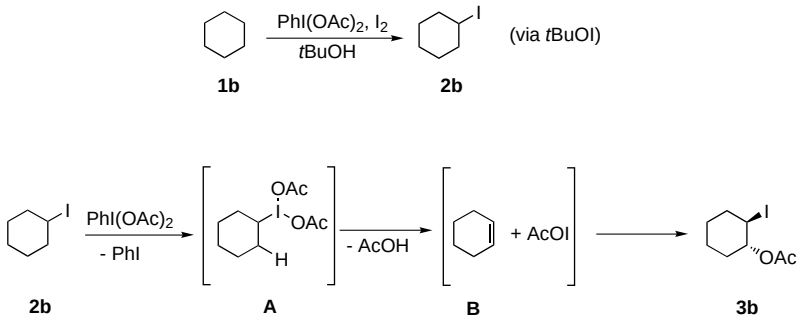
Table 2. Synthesis of 1-acetoxy-2-iodocycloalkanes **3** from cycloalkanes **1**.[a]

Entry	Cycloalkane (**1**)	$PhI(OAc)_2$[b]	Product (**3**)	Yield [%][c]
1	 **1a**	3.5	 **3a**	71
2	 **1b**	2	 **3b**	92
3	 **1c**	2	 **3c**	47
4	 **1d**	3	 **3d**	65

[a] All reactions performed with 1.1 equivalent of I_2. The alkane was used as solvent. Reaction time 14 h. [b] Molar ratio $[PhI(OAc)_2]$:*t*BuOH = 1:1. [c] Isolated yield referred to I_2.

transformation formally represents a direct and unprecedented diastereoselective 1,2-functionalization of an alkane. All the reactions were performed under ambient light at 40 °C (bath temperature) and different amounts of $PhI(OAc)_2$ were required to obtain fair to excellent yields of compounds **3**. When cycloheptane (**1c**) was employed as substrate in the reaction, a ring contraction was observed, affording the unexpected methylcyclohexane derivative **3c** in 47% yield (Table 2).

For the basis of a mechanistic proposal, an initial formation of intermediate species of hypoiodite nature, which result from the interaction of the $PhI(OAc)_2$–I_2 system and an alcohol, is widely accepted.[10] Thus, generation of *tert*-butylhypoiodite (*t*BuOI) could be reasonably invoked to promote the synthesis of the observed iodoalkanes **2** by a radical-chain mechanism.[4] The formation of the bifunctional derivatives **3** could be explained assuming a ligand transfer from $PhI(OAc)_2$ to the iodoalkane **2** previously formed,[11, 12] which gives rise to (diacetoxyiodo)alkane species (**A**; Scheme 2), which are in general unstable. An elimination reaction to generate an olefin (**B**), followed by addition of the acetylhypoiodite formed "in situ" would account for the observed *trans* diastereoselectivity in which 1-acetoxy-2-iodocycloalkanes **3** are obtained (Scheme 2).



Scheme 2. Proposed reaction mechanism.

In conclusion, a new method amenable for the selective mono- and bifunctionalization of alkanes has been described, under mild, simple and efficient conditions. The reported examples leading to the synthesis of bifunctional derivatives constitute the first diastereoselective vicinal activation reaction of a hydrocarbon. Further investigations concerning the interaction of iodine(III) species with alkanes are in progress.

Experimental Section

All reactions were carried out under a positive pressure of nitrogen. Alkanes **1** were dried under reflux over sodium, distilled under nitrogen, and purged with argon to remove oxygen traces prior to their use.

3b: Iodine (1.1 mmol, 280 mg) and *t*BuOH (2 mmol, 0.2 mL) were sequentially added to a suspension of $PhI(OAc)_2$ (2 mmol, 644 mg) in **1b** (25 mL). The resulting mixture was stirred at 40 °C (bath temperature) for 14 h. The mixture was allowed to cool and then quenched with sodium thiosulfate (5% solution in water, 25 mL). The mixture was transferred to a separating funnel, the aqueous layer was reserved and the organic one distilled under reduced pressure to recover excess **1b**. The distillation residue was diluted with diethyl ether (20 mL), mixed with the previously reserved aqueous layer and extracted. The aqueous phase was further extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with NaOH (5% solution in water, 2 × 40 mL), brine (2 × 40 mL), and dried over sodium sulfate. The solvent was removed at reduced pressure. The resulting liquid was further purified by column chromatography (hexane/ethyl acetate 25/1) to give **3b** as a pale yellow liquid (245 mg, 92%).

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[8] To our knowledge a direct and efficient iodination of toluene is almost without precedent. Previously, a

34 % yield was reported in the preparation of **2e** from **1e** and *t*BuOCl/HgI_2, see reference [4].
[9] None of the bifunctional derivatives **3** were observed when performing the reaction under photochemical conditions, even using an excess of $PhI(OAc)_2$. For instance, when **1a** was treated with $PhI(OAc)_2$ (2 equiv), I_2 (1.1 equiv), and *t*BuOH (2 equiv) under the influence of light at room temperature, only the formation of **2a** was observed after 8 h, the excess $PhI(OAc)_2$ was recovered.
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[12] We have observed that **2b** was cleanly converted into **3b** under comparable thermal conditions, thus providing additional evidence for the proposed mechanism.

Mechanism of the Transformation of Silica Precursor Solutions into Si-MFI Zeolite

Svetlana Mintova,* Norman H. Olson, Jürgen Senker, and Thomas Bein*

Dedicated to Professor Jens Weitkamp on the occasion of his 60th birthday

The mechanisms governing the transformation of precursor solutions or gels into zeolitic materials are still not fully understood.[1–5] The scientific challenge is to understand these mechanisms to enhance synthetic control for the design of new zeolite structures, and for the preparation of novel assemblies such as films, monoliths, and functional nanostructures.

The crystal growth of silicalite-1—a microporous polymorph with MFI topology—has received considerable attention because it can serve as model system for a fundamental understanding of the mechanism of zeolite formation.[6–9] The nanoscale organosilicate clusters in the precursor solutions used for the synthesis of nanosized MFI-type zeolite have been observed with techniques such as dynamic light scattering (DLS),[6] nuclear magnetic resonance (NMR),[7, 8] small-angle X-ray scattering (SAXS),[9, 10] and high-resolution transmission electron microscopy (HRTEM).[11–13] It appears that nanoscale species with a size of about 3–4 nm are formed in the precursor solutions before long-range order is established.[14, 15] Additional information about the structure, particle size, and shape of the silicate species in the MFI-precursor solutions containing organic additives was obtained by using NMR spectroscopy[16] and in situ SAXS measurements.[9, 10] These studies suggest that the aggregation of the primary units is an important step in the nucleation process, and that it depends on many factors, such as the alkalinity of the precursor solution, the type of silica source, and aging time. However, structural information regarding the initial framework species assembled from molecular precursors is still very limited.

In previous studies we have investigated the nucleation and growth processes of zeolites A (LTA) and Y (FAU) (using the tetramethylammonium (TMA) ion) by HRTEM.[11] It was observed that the crystalline structures nucleate in amorphous gel aggregates existing in the colloidal aqueous solutions, and that these gel aggregates are completely converted into crystalline products after extended reaction times.

Herein, we examine the formation of the colloidal precursor solution and the crystal growth of Si-MFI by in situ DLS combined with ^{29}Si solid-state NMR spectroscopy, HRTEM, and other techniques.

A clear precursor solution, prepared for the synthesis of Si-MFI zeolite, was aged at room temperature on an orbital shaker for 24 h (A24h) to 30 days (A30d). Samples were heated to 90 °C and then examined by in situ DLS measurements. A major advantage of the in situ study is the elimination of invasive procedures that may modify the crystallization process of the Si-MFI zeolite. Figure 1 shows

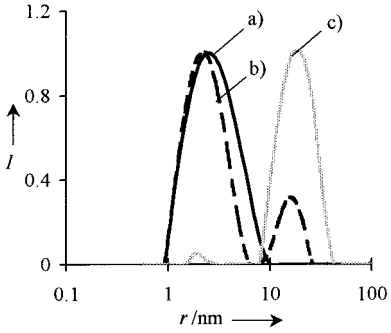

Figure 1. DLS data of TPA-silica precursor solutions: a) aged for 24 h (A24h) at room temperature, and after heating for b) 4 min (A24hH4m) and c) 6 h (A24hH6) at 90 °C. The distribution function analysis (DFA) is displayed as scattering intensity per unweighted particle size classes (I = scattering intensity).

the particle size (r) distribution of the precursor solution aged for 24 h (A24h), and for samples heated to 90 °C for 4 min (A24hH4m) and 6 h (A24hH6). Prior to heating, the presence of sub-colloidal particles with sizes in the range of about 1–10 nm is observed in the A24h sample. These particles are shown to be amorphous by X-ray diffraction. After hydrothermal treatment of solution A24h for only 4 min (Figure 1b), an increase of the scattering intensity is observed, due to the presence of a second generation of particles with mean radius of about 15 nm (sample A24hH4m; Figure 1b). The two particle populations present in these samples are quite diverse, the first having a mean radius of about 2.3 nm and the second having a radius of about 15 nm. By increasing the heating time from 4 min to 6 h (sample A24hH6; Figure 1c), the peak indicative for the presence of sub-colloidal

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