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## Synthesis and Photochemistry of 1-iodocyclohexene: Influence of Ultrasound on Ionic vs. Radical Behaviour

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**Abstract:** Simultaneous application of UV light and ultrasonic irradiation on the reaction mixture of 1-iodocyclohexene is reported. The irradiation of 1-iodocyclohexene was carried out in the with or without of zinc. The effect of ultrasound and mechanical stirring on solid-liquid system was compared.

**Introduction:** Alkyl halides exhibit competing radical and ionic photobehaviors<sup>1</sup>. Iodides gives predominantly ionic products. Process of irradiation involves the initial homolytic cleavage of the carbon-halogen bond followed by electron transfer within radical pair to generate ion pair. Irradiation of alkyl halides is convenient method for generation of carbocations. The corresponding vinyl cations are generated by irradiation of vinyl iodides. The products of photochemical reactions depend on the light intensity, as well as on effectivity of the stirring of the reaction mixture<sup>2</sup>. The application of the ultrasound, especially in heterogeneous reactions, causes the mechanical effect responsible for the mass transfer, that is, a thorough stirring of the reaction mixture as well as the activation of the surface of the solid reagent<sup>3,4,5</sup>. The second effect of ultrasound, the most pronounced in homogenous reactions, is caused by high temperature (up to 5000 K) and high pressure (up to 400 atm), which are involved in the collapsing bubbles (cavities) in the ultrasound field.<sup>3,4,5</sup> The main goal of this work was to examine simultaneous sonication and UV irradiation of 1-iodocyclohexene in methanol in absence/presence of zinc as iodine scavenger.

**Results:** The 1-iodocyclohexene **3** was prepared from ketone **1** by using some modifications of the general method of Pross and Sternhell<sup>6</sup> (Scheme 1).

### Scheme 1

#### Figure 1

Irradiation of 1-iodocyclohexene in methanol ( $\lambda = 254$  nm) during 60 min was monitored by gas-chromatography.

Irradiation of iodine **3** in methanol ( $\lambda = 254$  nm) afforded a mixture of the dimethyl ketal **6**, enol ether **5** and cycloalkene **4**<sup>7</sup>. Product **6** arises from acid-catalyzed addition of methanol to the nucleophilic trapping product **5**. Product **4** is radical-derived reduction product (Table 1, A).

### Scheme 2

CH <sub>3</sub> OH	time (min)	<b>3</b> (%)	<b>6</b> (%)	<b>5</b> (%)	<b>4</b> (%)

<b>A</b>	40	<b>33</b>	<b>23</b>	<b>18</b>	<b>26</b>
<b>B</b>	40	<b>10</b>	<b>23</b>	<b>25</b>	<b>42</b>
<b>C</b>	40	<b>24</b>	<b>20</b>	<b>35</b>	<b>22</b>
<b>D</b>	40	<b>4</b>	<b>15</b>	<b>41</b>	<b>40</b>

**Table 1:**  
**A** - irradiation  
**B** - simultaneous effect of ultrasound and irradiation  
**C** - irradiation in presence of zinc, mechanical agitation  
**D** - simultaneous effect of ultrasound and irradiation in presence of zinc  
 A rapid formation of **4** accompanied by a great decrease of **3** (Table 1,**B**) was observed after application of ultrasound.. The ultrasound significantly affect photobehaviour of this reaction predominantly in radical route. During mechanically stirring in the presence of zinc as an acid scavenger, the enol ether **5** was obtained mainly (Table 1,**C**). Ultrasound and irradiation in the presence of zinc caused rapid photodegradation of **3** and increase the ratio of the radical product **4D** to **4C** (Table 1).

**Conclusion:** The results obtained in our study (Table 1) showed that ultrasound affects photobehaviour of 1-iodocyclohexene in methanol. Ultrasound markedly influenced the lifetime of radical pair resulting from initial homolytic cleavage of the carbon-halogen bond. The increase of radical product **4** was observed. The ultrasound caused rapid photodegradation of starting iodide **3** (Table 1 **A,B**). The irradiation of 1-iodocyclohexene in methanol in presence of zinc increases the yield of **5** to compare with the yield after irradiation without zinc. The sonochemistry of zinc powder was investigated for few years ago<sup>8</sup>. Ultrasound in liquids creates acoustic cavitation. In the presence of fine powders, shockwaves and turbulent flow from cavitation resulted in interparticle collisions of solids. Such collisions occur with enough force to cause changes in morphology of powders. After application of ultrasound on zinc powder, dramatic changes in particle morphology was observed (Figure 3). The mechanical agitation keeps zinc particles smooth (Figure 2). The ultrasound makes the particles rough and grainy (Figure 3). The fragmentation of particle improved the transport of mass. Ultrasound and zinc positively contributed to production **4** and **5**. The rapid photodegradation of **3** was also observed. Mechanical stirring is more or less a local, being the most effective near the stirrer, but not so effective in the close proximity of the reactor walls. The sonochemical stirrig is evenly distributed over the entire reaction volume, as cavities are formed and implode at every place of the reaction mixture.<sup>4</sup>

**Figure 1:** Zn powder, mechanical stirring

**Figure 2:** Zn powder, ultrasound

## Experimental:

**General procedure:** Gas-chromatographic analyses were performed on a Agilent 6890N using capillary column HP-1 50m x 0.32mm ID with 1.05  $\mu\text{m}$  film thickness. The cyclohexene was used as a internal hydrocarbon standard. Proton NMR spectra were determined in chloroform-*d* with Varian Mercury Plus 300 MHz. Mass spectra were obtained by using a MSD-Agilent 5973 Network spectrometer.

**Preparation of 1-iodocyclohexene:** The iodide **3** was prepared from corresponding ketone **1** by using some modifications of general method of Pross and Sternhell<sup>6</sup>. Into-round-bottomed flask equipped with magnetic stirrer, condenser and additional funnel was placed 40.8 ml (0.84mol) of hydrazine hydrate. A solution of 6.4ml ( $6.15 \times 10^{-2}$ mol) of cyclohexanone in 35ml of absolute methanol was added very slowly!! (3 drops per min) to the hydrazin hydrate with vigorous stirring. When the addition was completed the reaction mixture was refluxed for 1h and then cooled to room temperature. The ethanol was evaporated and reaction mixture was washed with chloroform, aqueous sodium chloride and dried over anhydrous sodium sulphate. After filtration and evaporated of chloroform 6.3g (91%) of hydrazone **2** was obtain. <sup>1</sup>H NMR (300MHz,CDCl<sub>3</sub>): 4.88(s,2H,-NH), 2.28(m,2H,C1), 2.33(m,2H,C5),

2.23(m,4H,C2,C4), 1.73(m,2H,C3).

Iodine 27.4g (0.11mol) in 170.4ml dry ether was added dropwise to a stirred solution of 41.6 ml (0.29mol) triethylamine and 6g (0.05mol) of hydrazone **2** in 18.1ml of dry ether at room temperature. The colour of the reaction mixture was changed from yellow to brown after addition of the iodine solution. The reaction was instantaneous, but stirring continued for a further 20min. The reaction mixture was diluted by adding 150 ml of dry ether and washed with saturated aqueous sodium sulphite, 3N HCl, saturated aqueous sodium bicarbonate and aqueous sodium chloride. The organic layer was then dried over sodium sulphate, evaporated to give 1,37g (13%) of product **3** which was purified by chromatography (silicagel, mesh 100-250, petroleum benzene 40-60°C). <sup>1</sup>H NMR (300MHz,CDCl<sub>3</sub>): 6.33(sep.,1H,CH), 2.5(m,2H,C6), 2.1(m,2H,C3), 1.7(m,4H,C2,C6).

**Irradiations:** The photochemical reactor allowing simultaneous ultrasound irradiation was used. A sandwich piezoelectric transducer (50W, 20kHz, intensity≈16W.cm<sup>-2</sup>) was attached by an epoxy resin to the bottom of normal photochemical reactor with internally water-cooling (50mm diameter, 40ml volume). Irradiations of **3** in methanol (c = 1.63x10<sup>-3</sup>mol/l) were carried out with 4W (254nm) low pressure mercury lamp. During irradiation, the solution was flushed with argon.

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