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Ultrasound-Mediated Rearrangement of β-Ionone to 1,1,6-Trimethyl-1,2,3,4-Tetrahydronaphthalene.

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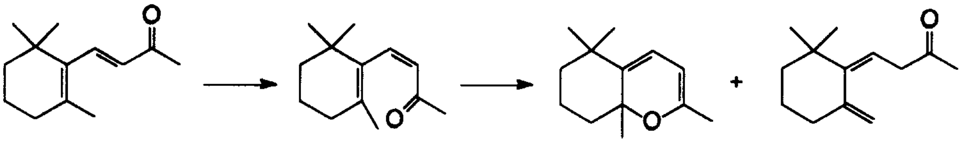
Abstract: The rearrangement of β-ionone in $CHBr_3$ to 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene was studied under sonochemical conditions. Trapping experiments showed ultrasound to induce the generation of bromine radicals from $CHBr_3$ that abstracted hydrogen from the solvent to yield HBr. The hydrogen bromide catalyses the cyclisation of β-ionone.

Sonochemistry is becoming increasingly important for a variety of synthetic organic reactions that are either facilitated by sound waves, or otherwise unattainable.[1] Most of the ultrasound accelerated reactions concern heterogeneous solid-liquid reaction systems involving metals in which the sonochemical benefit can at least partly be attributed to the removal of passivating surface coatings.[2] A clearcut example of homogeneous sonochemistry is the (*E*)/(*Z*) isomerization of substituted alkenes mediated by bromine radicals generated from alkylbromides.[3] In an attempt to establish whether this reaction is restricted to relatively simple substrates or suitable for general application, the bromine radical mediated isomerization of β-ionone (**1**) was investigated.

Upon hν irradiation, (*E*)-β-ionone isomerizes to (*Z*)-β-ionone that rearranges to a mixture of a bicyclic pyran and *(Z)-retro*-γ-ionone (eq 1).[4]

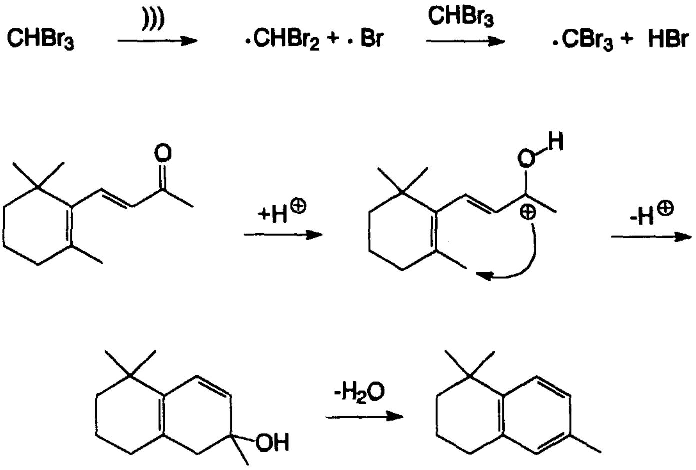


equation 1

On the other hand, thermal reaction of **1** with iodine produces 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene[5] in what might be considered a radical reaction, although the exact mechanism has yet to be elucidated. The naphthalene derivative is a valuable intermediate in the synthesis of herbicidal compounds,[5] natural flavours[6] and nitro musks.[7]

Sonication of 0.1 M solutions of 1 in $CHBr_3$ at 20 °C showed rapid consumption of the starting material. After 3 h only trace amounts of 1 could be detected (GC) together with a single product, and sonication was stopped. The product formed proved to be unstable under the applied reaction conditions (even without ultrasound)[8] and slowly underwent further reaction to yield a single final product that was identified by MS and ^{1}H- and ^{13}C-NMR as 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene (**2**).[5b-c,6] Pyran, *retro*-γ-ionone or products resulting from the addition of bromine radicals to the C=C bonds of 1 could not be detected. Apparently, bromine radical induced (*E*)/(*Z*) isomerization of 1 does not occur.

Two experiments were carried out to elucidate the mechanism of the rearrangement of 1. Support for the intermediacy of radical species comes from an experiment in which one equivalent of the radical trap 4-hydroxy-2,2,6,6-piperidinyloxy (4-hydroxy-TEMPO) was added. Only after the trap had completely disappeared (1 h; GC) did the concentration of 1 start to decrease. Since in the absence of either $CHBr_3$ or ultrasound no reaction was observed, bromine radicals are the most likely primary radical species involved.[3b-c] The bromine radical could subsequently abstract a hydrogen atom from a second solvent molecule to produce HBr[9] that catalyses the rearrangement of 1 to yield **2** *via* an enol intermediate.[5b] To test this hypothesis, a rearrangement reaction was carried out in which one equivalent of triisobutylamine was added[10]. Addition of triisobutylamine has the same effect as the addition of 4-hydroxy-TEMPO: the concentration of 1 only diminished after all the amine had been consumed (1 h; GC). These observations make the acid induced rearrangement the most likely pathway (Scheme 1).



SCHEME 1

This conclusion was further supported by an experiment in which **1** was reacted with gaseous HBr (3 eq.) in $CHBr_3$. Product **2** was formed at virtually the same rate and in the same yield as in the sonochemical reaction.

Other reactions that could profit from the *in situ* generation of HBr from insonated $CHBr_3$ are currently under investigation.

EXPERIMENTAL

General Procedures. All insonated reactions were carried out with a Heat Systems Sonicator Ultrasonic Liquid Processor Model XL-2020 (20 kHz, 550 W, 1.27 cm tip, power output 17 W/cm^2 for all experiments[13]) and thermostated at 20 ± 1 °C. All reactions were carried out under argon atmosphere. Products were characterised by comparison of their NMR spectra with those found in the literature.[5b-c]

Rearrangement of β-ionone (1). A solution of **1** (1.057 g, 5.50 mmol) and eicosane (0.292 g, 1.03 mmol; internal standard) in 55 mL $CHBr_3$ was insonated for 3 h. The reaction mixture was then allowed to stand at 20 °C until the reaction was complete. Samples were taken at regular intervals and analysed by GC. After 24 h the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (100% hexanes) to afford **2** (0.757 g, 79%).

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8. All attempts to isolate this intermediate have failed so far. However, GC-MS analysis of the crude reaction mixture has provided strong indications that the compound can be identified as 2,5,5-trimethyl-1,2,5,6,7,8-hexahydronaphthalen-2-ol, i.e. the cyclised intermediate from Scheme I.
9. The formation of HBr from insonated $CHBr_3$ has been observed before. See: Suslick, K.S.; Schubert, P.F. *J. Am. Chem. Soc.* **1983**, *105*, 6042.
10. Although sonochemical reactions are quite sensitive to the addition of liquid reagents, the low vapour pressure of triisobutylamine[11] together with its low concentration make it unlikely that the presence of the amine influences cavitation significantly.[12]
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13. Measured by calorimetry. See also ref. 3c.

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