## A Mild and Efficient Sonochemical Bromination of Alkenes Using Tetrabutylammonium Tribromide

Jacques Berthelot<sup>\*</sup>, Yamina Benaminar and Catherine I ange

Laboratoire de Chimie Organique Structurale, Bâtiment F Boîte 45, associé au CNRS Universite Pierre et Marie Curie, 4 Place Jussieu 75230 Paris Cédex 05, France

Key words bromination, tripromide, sonication, alkenes, vicinal dibromoalkanes

Abstract : The bromination of substituted alkenes using tetrabutylammonium tribromide can be effectued under mild conditions with ultrasonic irradiation. This process gives quantitatively the corresponding vicinal dibromide in high yield.

Bromination of substituted alkenes with tetrabutylainnionium tribromide (TBABr<sub>3</sub>) is one of the easiest methods for the preparation of vicinal dibromoalkanes<sup>1,2</sup>. TBABr<sub>3</sub><sup>3</sup> reacts under simple stirring at 100m temperature in aprotic solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN) with aryl or alkyl alkenes and leads to the corresponding vicinal dibromides. The stereochemistry of the addition of the two bromine atoms is anti<sup>1,2</sup>.

$$RCH = CHR' + TBABr_3 - RCH - CHR' + TBABr_3$$

In a previous study we have reported new data for a very easy electrochemical monitoring of the amount of reacted TBABr<sub>3</sub><sup>4</sup>. Now, we describe a new process for this bromination, where TBABr<sub>3</sub> reacted under ultrasonic irradiation<sup>5</sup>. The reaction is carried out in a standard ultrasonic cleaning bath (50 KHz) at room temperature using  $2.10^{-3}$  mole of alkene and  $2.10^{-3}$  mole of TBABr<sub>3</sub> in 20 ml of solvent (CHCl<sub>3</sub>) The red-colored solution rapidly turned yellowish, then colourless. The bromination is then finished. Voltammetric monitoring<sup>4</sup> confirmed this result. The solution was worked up as already described<sup>1</sup>. All the vicinal dibromoalkanes were identified by comparison (m.p. or b.p., <sup>1</sup>H n.m.r. and mass spectra) with authentic samples. Their purities were determined by g1c analysis (CP SIL5). The different results are reported in Table 1.

| Table 1 : Bromination of alker |
|--------------------------------|
|--------------------------------|

| Alkene  | under stirring  |  | under sonication                                    |  |
|---|---|--|---|--|
|   | Time (min)  | Yield (%) <sup>a</sup>                       | Time (min)  | Yield (%) <sup>a</sup>   |
| Cyclohexene<br>1-Methyl-1-cyclohexene<br>Trans-2-hexene<br>Styrene<br>Trans-Stilbene<br>1-Octene<br>Trans-2-Octene<br>Trans-4-Octene<br>Benzylideneacetophenone | $ \begin{array}{c} 1\\ 5\\ 1\\ 20\\ 700\\ 20\\ 5\\ 5\\ 1500\\ \end{array} $ | 97<br>98<br>95<br>78<br>91<br>93<br>93<br>66 | < 0.1<br>1<br>0.3<br>2<br>120<br>2<br>2<br>2<br>240 | 99<br>99<br>98<br>99<br>98<br>98<br>98<br>98<br>98<br>98<br>98<br>98 |

## a) isolated yield

## We can observe that :

- In every case the bromination was accelerated under ultrasonic irradiation and the yields were quantitative. These results are particulary interesting when the bromination was very slow with stirring. The vicinal dibromoalkanes obtained remained unaffected under sonication. The stereochemistry of the addition is the same : the trans-alkenes utilized (trans-2-hexene, trans-stilbene, trans-2-octene, trans-4-octene) afforded the meso or the dl erythro dibromoalkanes.

- No effect of solvent was noted under sonication. Bromine was apparently decomposed under ultrasonic irradiation into the two (Br.) radicals<sup>5</sup>. TBABr3, on the contrary, was not deteriorated under sonication and the stereoaddition of this bromination remained anti.

As this bromination is a homogeneous reaction ultrasonic irradiation could have a direct chemical influence<sup>6</sup>. Applications to more complicated structures are presently under investigation.

In conclusion the use of ultrasound, when applied to the bromination of alkenes by TBABr<sub>3</sub>, seems to be a very interesting process to form easily, under mild conditions, the corresponding vicinal dibromocompounds. The possible extensions to other types of additions are currently under study.

Acknowledgements : We thank Professor J-J. Basselier for stimulating discussions.

## **References and Notes :**

- 1) Berthelot J.; Fournier M., J. Chem. Ed., 1986, 63, 1011.
- 2) Belluci G.; Chiappe F.; Marioni C., J. Am. Chem. Soc., 1987, 109, 515.
- 3) TBABr3 is available from Janssen Chimica.
- 4) Berthelot J.; Desbene P-L.; Desbene-Monvernay A.; Basselier J-J., Analusis, 1987, 15, 22.
- 5) For extensive recent review of ultrasound reactions see :
  a) Einhorn C.; Einhorn J.; Luche J.L., Synthesis, 1989, 787.
  b) Luche J.L.; Einhorn C., Janssen Chimica Acta, 1990, 8, 8.
- 6) Luche J.L.; Einhorn C.; Einhorn J.; Sinisterra-Gago J.V., Tetrahedron Lett., 1990, 31, 4125.

(Received in France 16 May 1991)