

## Trimethyloxosulphonium Chloride from the Iodide through Ion Pair Extraction

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Trimethyloxosulphonium halides are important reagents as precursors of dimethyloxosulphonium methylid.<sup>1</sup> Whereas the synthetic procedure yields the iodide,<sup>2</sup> the trimethyloxosulphonium chloride has the advantage of being more soluble in tetrahydrofuran. The preparation of the ylid is thus made possible in this solvent.

The conversion of the iodide to the chloride has been carried out with elemental chlorine.<sup>1</sup> The same change of anion can be more simply and rapidly achieved using ion pair extraction. If trimethyloxosulphonium iodide and an equimolar amount of a suitable quaternary ammonium chloride, e.g., the benzyltributylammonium salt, are distributed between dichloromethane and water, the latter will contain trimethyloxosulphonium chloride, whereas the organic phase will contain benzyltributylammonium iodide. Since iodides are extracted into dichloromethane and similar solvents a thousandfold better than the corresponding chlorides,<sup>3</sup> the ion exchange is practically complete.

The reason for choosing benzyltributylammonium chloride in the present work was that this salt could be simply prepared from inexpensive starting materials, tributylamine and benzyl chloride, in acetonitrile. Kantor and Hauser have reported<sup>4</sup> that this quaternization fails in refluxing benzene or in the absence of solvent. An early report<sup>5</sup> of a successful preparation of the salt in benzene solution could not be reproduced by us and is probably erroneous. The melting point, 185 °C, given in Ref. 5 disagrees with the one found in the present work, 162–164 °C. To obtain a good yield in acetonitrile, one week's refluxing was necessary.

*Experimental.* Benzyltributylammonium chloride. A mixture of 185.4 g (1 mol) of freshly distilled tributylamine, 139.0 g (1.1 mol) of benzyl chloride, and 300 ml of acetonitrile, purified according to O'Donnell and his co-workers,<sup>6</sup> was kept at gentle reflux for one week. Most of the acetonitrile was removed at aspirator vacuum, and 500 ml of dry ether was added, which caused the quaternary salt to precipitate. This was filtered off and washed with dry ether until colourless (ca. 500 ml).

Drying *in vacuo* yielded 268.2 g (86 %) of crude product. Recrystallization from ethyl acetate containing some ethanol gave an odourless product, m.p. 162–164 °C (unchanged on further recrystallization). The recovery was only 60 %. Argentometric titration showed the purified salt to contain 11.3 % of chloride; calc. for C<sub>19</sub>H<sub>34</sub>NCl, 11.4 %.

*Trimethyloxosulphonium chloride.* A solution of 15.6 g (0.05 mol) of benzyltributylammonium chloride in 100 ml of water was shaken with 10.2 g (0.05 mol) of trimethyloxosulphonium iodide<sup>2</sup> and 75 ml of dichloromethane until a clean two-phase liquid system was obtained. The aqueous phase was washed with 50 ml of dichloromethane and evaporated, first at aspirator vacuum and then for several hours at an oil pump until constant weight. A quantitative yield of trimethyloxosulphonium chloride was obtained (5.6 g), m.p. 222–223 °C, lit.<sup>1</sup> 220–222 °C. Iodide was absent as indicated by a spot test with 30 % hydrogen peroxide. From the 60 MHz <sup>1</sup>H NMR spectrum, recorded in deuterium oxide solution, it could be concluded that a trace (less than 0.2 mol %) of benzyltributylammonium ion was present which can be disregarded in synthetic use.

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