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11th Paul Walden Symposium on Organic Chemistry

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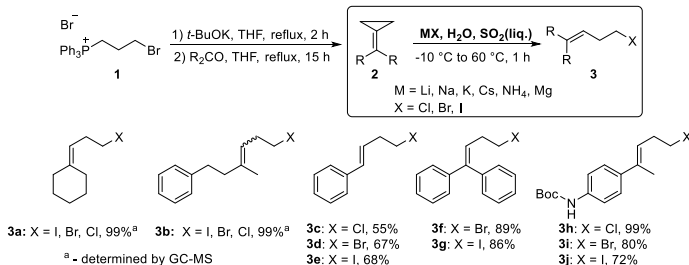
Addition of halides to cyclopropylenes in liquid SO₂

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Methylenecyclopropanes (MCPs) are easily accessible yet highly strained and reactive building blocks.¹ MCP can be readily opened under transition metal or Lewis acid catalyzed conditions.² We have hypothesized that a highly polar and Lewis acidic reaction medium could facilitate the ring opening of MCPs with simple nucleophiles. We have recently shown that liquid sulfur dioxide perfectly fulfils the aforementioned solvent requirements.³ Additionally, it dissolves well inorganic salts.⁴ Here we report ring opening of MCPs in liquid SO₂ with I and II group metal halides (**Scheme 1**). The substrates **2** were obtained in reactions between ketones and (3-bromopropyl)triphenylphosphonium bromide (**1**). Practically all tested I and II group metal (and ammonium) halides were able to open benzaldehyde-derived MCP, which was used as the test substrate. The activity order of cations was found to be: Li⁺ > Mg²⁺ > Cs⁺ > K⁺ > Na⁺ > NH₄⁺. The activity order of anions was found to be: I⁻ > Br⁻ > Cl⁻. Various substituted MCP were reacting with the aforementioned halides and products **3a-j** were obtained with good to excellent isolated yields. Gratifyingly, the developed method is sufficiently mild against the acid-labile protecting groups. Thus Boc-protected substrate provided products **3h-j** in excellent yields. This can be explained by the fact that the equilibrium SO₂ + 2H₂O → H₃O⁺ + HSO₃⁻ is not efficiently shifted to the right in the liquid SO₂ medium.^{3a} Hence, the water traces in liquid SO₂ form a less acidic medium if compared with the SO₂ solution in water.

**Scheme 1.** Synthesis of homallylic halides from ketones.

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