Synthesis of Alpha-pinene Peroxide from Alpha-pinene Using Singlet Oxygen [O_2 ($^1\Delta_{2g}$)]

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Alpha-pinene is a naturally occurring monoterpene found in the essential oils of many plants, and its oxidation using singlet oxygen [O_2 ($^1\Delta_{2g}$)] produces alpha-pinene hydroperoxide and hydroxide, compounds with potential biological activities. Given that alpha-pinene's anxiolytic activity, its oxidized derivatives may exhibit similar or amplified effects, warranting further investigation. A previous report on computational work shows that singlet oxygen can be used to get the peroxide from alpha pinene. This study aims to synthesize alpha pinene peroxide and hydroxide using singlet oxygen ($^1O_2$) generated with a light source and a photosensitizer. Initially, (1S,5S)-2,6,6-trimethylbicyclo [3.1.1] hept-2-ene ((−)-α-pinene) was characterized using ^{1}H NMR spectroscopy to confirm its structural integrity. Oxidation was performed using 1 cm^3 (0.858 g) of alpha-pinene and 0.001 g of methylene blue photosensitizer in 50 mL of chloroform, with a 200W tungsten halogen lamp radiation source and a continuous flow of oxygen. The reaction mixture was irradiated for 6 hours, and the reaction progress was monitored with Thin Layer Chromatography (TLC), indicating the presence of the alpha pinene peroxide and hydroxide with unreacted alpha-pinene. The products were isolated via column chromatography using a hexane-ethyl acetate (1:1) solvent system and characterized by ^{1}H NMR and IR spectroscopic techniques. The isolated alpha pinene peroxide yield was 0.13 g (18.6%). Important ^{1}H NMR chemical shifts were at ppm 7.99 (OOH), 5.07 and 4.83. IR key absorption bands at 844.08 cm^{-1} (O-O stretching vibrations), 1024.99 cm^{-1}(C-O stretching) and 3339.75 cm^{-1}(O-H stretching). The major product alpha pinene hydroxide yield was 0.526 g (61.3%) where the ^{1}H NMR 7.99 peak and the IR 844.08 cm^{-1} peak corresponding to the peroxide was absent. Analysis confirmed successful oxidation and as expected pinene peroxide was converted to the more stable pinene hydroxide. The method, utilizing methylene blue and a tungsten halogen lamp, proved effective for this oxidation process. In conclusion, alpha-pinene peroxide was synthesized and characterized, however further studies are in progress to force the reduction of pinene peroxide to hydroxide to get the more stable hydroxide in a better yield.

Keywords: *Alpha-Pinene Peroxide, Singlet Oxygen, Methylene Blue, Tungsten Halogen Lamp*