**Significance:** Commercially available anatase TiO₂ nanoparticles promoted the hydroalkylation of alkenes bearing electron-withdrawing groups with carboxylic acids under 390 nm light irradiation to give the corresponding hydrocarbons in up to 91% yield (eq. 1).

**Comment:** Mechanistic studies indicated that alkyl radicals were generated by decarboxylation of the carboxylic acids promoted by TiO₂ (eq. 2). The catalytic activity of TiO₂ was superior to that of various heterogeneous semiconducting photocatalysts such as ZnO, WO₃, or CdS.