

X. DU, H. FAN\*, S. LIU, Z. C. ZHANG\* (DALIAN INSTITUTE OF CHEMICAL PHYSICS AND CHANGZHOU UNIVERSITY, P. R. OF CHINA)

Selective Nucleophilic  $\alpha$ -C Alkylation of Phenols with Alcohols via Ti=C $\alpha$  Intermediate on Anatase TiO<sub>2</sub> Surface

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# Nucleophilic C-Alkylation of Phenols with Alcohols Promoted by Anatase TiO<sub>2</sub>

Category

Polymer-Supported Synthesis

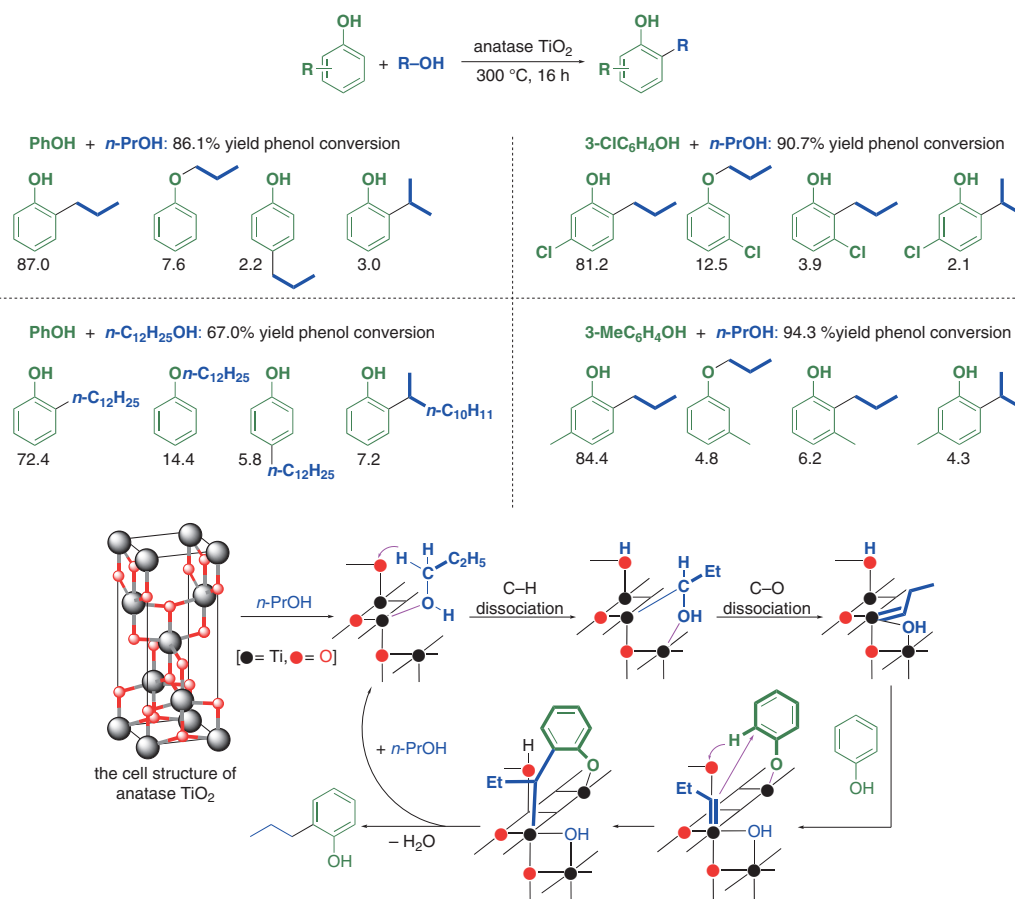
Key words

aromatic alkylation

anatase TiO<sub>2</sub>

nucleophilic aromatic functionalization

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**Significance:** C-alkylation of phenols with alcohols was promoted by anatase TiO<sub>2</sub> at 300 °C. Phenol reacted with *n*-propyl alcohol to give 2-propylphenol with 87% selectivity. Rutile TiO<sub>2</sub>, a stable polymorph of titania, did not promote the C-alkylation (ca. 0% phenol conversion). Phenols bearing 3-chloro and 3-methyl substituents showed a similar trend of selectivity for the alkylation, although they have opposite electronic effects.

**Comment:** DFT calculations as well as experimental observations indicate that the main reaction pathway of C-alkylation is different from the conventional Friedel-Crafts alkylation. The authors have proposed that the reaction proceeds via a Ti=C $\alpha$  intermediate which reacted with a Ti-activated phenol nucleophilically at the *ortho*-position.

SYNFACTS Contributors: Yasuhiro Uozumi, Shintaro Okumura  
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