

OXIDATION OF PROPYLENE BY BENZOYL PEROXIDE TO ALLYL  
ACETATE CATALYZED BY A PALLADIUM CLUSTER AND Pd BLACK

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The reaction of olefins with acyl peroxides both in the absence [1] and in the presence of transition-metal compounds [2] is usually nonselective and results in the formation of an extensive set of products. We discovered that a cluster with the composition  $\text{Pd}_4\text{phen}(\text{OAc})_2$  (I, phen = 1,10-phenanthroline) [3] and Pd black catalyze the selective liquid-phase oxidation of propylene (II) by benzoyl peroxide (III) under anaerobic conditions:



In a typical experiment up to 4 moles of (III) were introduced per g-atom of Pd. The only product of the oxidation of (II) in an AcOH solution at 60°C and 0.1 MPa [the extent of conversion of (III) was 90-95%] is allyl acetate, whose yield as calculated for the reacted (III) is  $100 \pm 5\%$  in the case of catalysis by cluster (I) and  $70 \pm 5\%$  in the presence of Pd black [in the latter case, about 30% of (III) decomposes into PhCOOH and  $\text{O}_2$ ]. The data obtained confirm the hypothesis advanced in [4] regarding the possible participation of  $\text{H}_2\text{O}_2$  and other peroxide compounds in the oxidative acetoxylation of unsaturated hydrocarbons by molecular  $\text{O}_2$  on Pd clusters. Reaction (1) is the first example of the selective oxidation of olefins by peroxides to allyl ethers on clusters or metallic Pd catalysts in the presence of carboxylic acids.

LITERATURE CITED

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