Effect of anchimeric assistance in the reaction of triphenylphosphine with α , β -unsaturated carboxylic acids

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Abstract

Quaternization of triphenylphosphine with maleic and cis-aconitic acids is strongly accelerated by participation of the cis-carboxyl group in stabilization of the phosphonium zwitterion intermediate by intramolecular hydrogen bonding, in spite of steric hindrance by the acid's reaction center. A similar effect for trans-isomeric acids is not observed, which can be rationalized on the basis of spatial structures of the generated zwitterions, implying an electrostatic interaction between the phosphonium center and carbonyl oxygen atom. The effect of anchimeric assistance decreases when the intramolecular hydrogen bonding disfavors attack of the phosphine on the sterically less hindered carbon atom of the C=C bond, as observed for cis-aconitic acid. © 2014 Wiley Periodicals, Inc.

http://dx.doi.org/10.1002/kin.20842