SELECTIVE CATALYTIC ADDITION OF HYDROGEN HALIDE AND CARBOXYLIC ACIDS AND PHENOLS TO METHYL ESTERS OF 1-ALKYL-3-CYCLOPROPENECARBOXYLIC ACIDS

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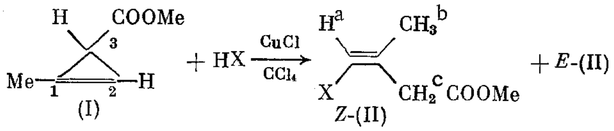
According to Ege and Hahn [1], acids cause the conversion of esters of cyclopropenecarboxylic acids for furan derivatives or nonselective ring opening of these esters with the formation of various alkenecarboxylic acid esters.

We have found a selective catalytic addition of hydrogen halide and carboxylic acids as well as of phenol to the methyl ester of 1-methyl-3-cyclopropenecarboxylic acid (I) in the presence of CuCl at the $C^2—C^3$ bond to form the methyl esters of Z- and E-isomers of 4-substituted 3-methyl-3-butene-1-carboxylic acids (II) in 65-92% yields.



X = Cl, Br, OAc, OCOCH=CH$_2$, OPh.

The experiments were carried out at 15-25°C. A homogeneous solution of 1-5 mole % 1:2 complex of CuCl with $MeC\equiv CSiMe_3$ was added to a solution of (I) and HX taken in 1:1.1 mole ratio in CCl_4.

The IR spectra of all (II) had a weak band at 1630-1680 cm^{-1} and strong band at 1735-1745 cm^{-1} characteristic for isolated C=C and C=O bonds, respectively. The PMR spectrum of (II) has signals at δ 5.9-7.0, 3.5-3.7, and 1.95-2.05 ppm corresponding to H^a m ($^4J > 1.5$ Hz), OCH_3 s and H^b m ($^4J < 1.5$ Hz). The H^c protons (m, $^4J < 1.5$ Hz) differ in the Z- and E-isomers by about 0.2 ppm which permits quantitative determination of the isomer ratio of (II) relative to the intetral intensities of these signals.

The E-isomer forms predominantly in the reaction of (I) with hydrogen halide and carboxylic acids (the E/Z ratio varies from 1.25:1 to 5:1), while the Z-isomer predominates in relations with phenol (the E/Z ratio of 1:3). The isomers of (II) are stable in the presence of CuCl and the acids studied and do not interconvert. In the absence of CuCl, starting esters (I) are not altered at 20-25°C even upon contact with HCl over many hours. The methyl esters of 1-propyl- and 1-amylcyclopropenecarboxylic acids react analogously with hydrogen halide and carboxylic acids and phenol.

Comparison of these results with data for the catalytic isomerization of esters of cyclopropenecarboxylic acids to alkoxyfuranes [2] and reactions with norbornadiene [3], CuCl and methanol [4] indicates that the major driving force for these reactions is the coordination of the cyclopropenes by the cuprous ion leading to a weakening of the $C^2—C^3$ bond. The subsequent transformations are a function of the extent of ionization of this bond and the nature of the reagent.

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