

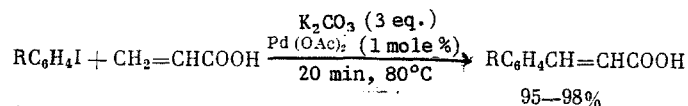
SYNTHESIS OF SUBSTITUTED CINNAMIC ACIDS BY THE HECK REACTION  
IN AQUEOUS MEDIA

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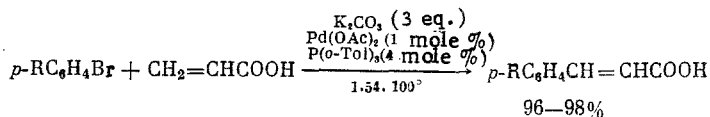
The reaction of aryl halides with olefins catalyzed by palladium complexes (Heck reactions) is usually carried out in anhydrous solvents in the presence of bases [1-3].

We have shown that water-soluble aryl iodides react with acrylic acid in water in the presence of  $K_2CO_3$  as the base to form a quantitative yield of the corresponding cinnamic acids.



R = m-HOOC (I), p-HO (II).

Other water-soluble bases such as  $Na_2CO_3$ , NaOH, and KOH may be used instead of  $K_2CO_3$ . The base strength in the case of (II) should be sufficient for the formation of the phenolate anion. In the case of water-insoluble aryl halides, the reaction is carried out in the presence of 20 vol. % HMPA. The reaction proceeds heterogeneously and requires rapid stirring.



R = Me, MeO.

**Method 1.** A sample of 2.07 g (15 mmoles)  $K_2CO_3$ , 1.24 g (5 mmoles) m-HOOC $C_6H_4I$ , 0.51 ml (0.54 g, 7.5 mmoles)  $CH_2=CHCOOH$ , and 0.0112 g (0.05 mmole)  $Pd(OAc)_2$  were dissolved in 5 ml water in an argon atmosphere. The mixture was stirred at  $80^\circ C$  for 20 min. Palladium black was filtered off and the filtrate was acidified by the addition of HCl. The precipitate formed was filtered off, washed with water, and dried to give 0.94 g (98%) m-carboxycinnamic acid, mp  $262-264^\circ C$ .

**Method 2.** A sample of 0.061 g (0.2 mmole)  $P(o\text{-}Tol)_3$  and 0.0112 g (0.05 mmole)  $Pd(OAc)_2$  were dissolved in 1 ml HMPA in an argon atmosphere. After 5 min, 4 ml water, 2.07 g (15 mmoles)  $K_2CO_3$ , 0.51 ml (0.54 g, 7.5 mmoles)  $CH_2=CHCOOH$ , and 0.64 ml (0.935 g, 5 mmoles) p- $CH_3OC_6H_4Br$  were added. Stirring was continued for 1.5 h at  $100^\circ C$ . The separation procedure was as in method 1. The yield of p-methoxycinnamic acid was 0.87 g (98%), mp  $171-173^\circ C$ .

LITERATURE CITED

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