PALLADIUM-CATALYZED ARYLATION OF ACRYLIC ACID BY DIARYLIODONIUM SALTS IN WATER

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Uchiama et al. [1] have shown that the reaction of diaryliodonium salts with olefins catalyzed by palladium compounds proceeds in anhydrous organic solvent in the presence of base (sodium acetate) to give the product of the arylation of the olefin and an aryl iodide. Alkenyl(aryl)iodonium salts react similarly [2].

We have found that this reaction may be carried out in an aqueous medium in the presence of catalytic amounts of $Pd(OAc)_2$ and Na_2CO_3 as the base. Acrylic acid is arylated by bis(*m*-nitrophenyl)iodonium salts at 20°C to give *m*-nitrocinnamic acid and *m*-nitroiodobenzene:

$$(m\text{-}NO_2C_6H_4)_2I^+X^- + CH_2{=}CHCOOH \xrightarrow[H_2O,\ 20^\circ C,\ 1h]{Pd(OAc)_2} m\text{-}NO_2C_6H_4CH{=}CHCOOH + m\text{-}NO_2C_6H_4I \quad (1)$$

The yield of *m*-nitrocinnamic acid was 97% when $X^- = HSO_4$ and 80% when $X^- = BF_4$.

Since iodoarenes, in turn, may undergo the Heck reaction, carrying out reaction (1) at 100°C permitted use of both aryl substituents of the diaryliodonium salt:

$$Ar_2I^+X^- + 2CH_2{=}CHCOOH \xrightarrow[H_2O,\ Na_2CO_3]{Pd(OAc)_2} 2ArCH{=}CHCOOH \quad (2)$$

$X^- = HSO_4$ and BF_4.

When Ar = *m*-$NO_2C_6H_4$, the reaction time was 0.25 h and the yield was 97%. When Ar = Ph, the reaction time was 3 h and the yield was 83%. When Ar = *p*-$MeOC_6H_4$, the reaction time was 3 h and the yield was 90%. When Ar = Mes, the reaction time was 10 h and the yield was 50%.

In the case of asymmetrical methylphenyliodonium tetrafluoroborate, cinnamic acid (47% yield) and iodomesitylene were formed under the same conditions.

In a typical experiment, a sample of 0.2 ml (2 mmoles) acrylic acid, 6 mmoles Na_2CO_3, and 0.0044 g (2 mole %) $Pd(OAc)_2$ were added under argon to 0.468 g (1 mmole) bis(*m*-nitrophenyl)iodonium bisulfate in 4 ml water and stirred for 15 min at 100°C. After acidification, the precipitate was filtered off and recrystallized from ethanol. The yield of *m*-nitrocinnamic acid was 0.181 g (94%), mp 200°C.

REFERENCES

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