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SHORT COMMUNICATIONS

Microwave Enhancement of Arylation of Activated Olefins with 4-Bromoacetophenone

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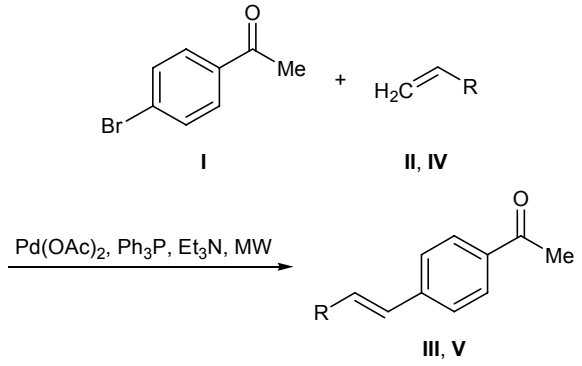
Palladium-catalyzed arylation and vinylation of olefins (Heck reaction) are important reactions in organic synthesis [1, 2]. In most cases, under classical conditions (closed system, no solvent, temperature 100–120°C) complete substrate conversion is attained in several hours to several days [3]. Attempts to carry out the reaction at a higher temperature resulted in decomposition of the catalytic system and formation of by-products. In the recent time, examples of successful application of microwave irradiation to accelerate Heck reactions in polar solvents have been reported [4–8].

We compared the results of arylation of some activated olefins with 4-bromoacetophenone (**I**) under classical solvent-free conditions and under microwave irradiation. The reaction mixtures were heated in a thermostat (temperature range 85–140°C) and in the active zone of a microwave furnace (40–300 W). The reaction of 4-bromoacetophenone (**I**) with methyl acrylate (**II**) in both cases gave methyl (2*E*)-3-(4-acetylphenyl)acrylate (**III**) as the only product. The spin–spin coupling for the olefinic protons in **III** was larger than 16 Hz, which unambiguously indicated *trans* configuration of the double bond. Ketone **I** reacted with styrene **IV** in a similar way, yielding exclusively 1-{4-[(*E*)-2-phenylvinyl]phenyl}ethan-1-one (**V**).



I **II**, **IV** **III**, **V**

II, **III**, R = COOMe; **IV**, **V**, R = Ph.

At temperatures below 100°C the reactions occurred at a low rate, and the yields were almost quantitative (calculated on the reacted compound **I**). The reaction rate considerably increased when the temperature was raised above 110°C, but the selectivity of the process simultaneously decreased. Above 140°C, side processes became predominating. Thus the optimal temperature in the classical procedure is ~100°C; it ensures high yields of the target products and acceptable reaction time.

By varying the microwave irradiation power and other conditions we succeeded in considerably shortening the reaction time, the high selectivity being retained, without using polar solvents. At an MW power of 140 W, the complete conversion of 4-bromoacetophenone (**I**) was attained in all cases within 10 min, and the yields of products **III** and **V** were comparable with those obtained under conventional heating at 100°C over a period of 15 h.

Arylation of activated olefins with 4-bromoacetophenone (*general procedure***).** A 10-ml thick-walled ampule was charged with 1.990 g (10 mmol) of 4-bromoacetophenone (**I**), 12.5 mmol of methyl acrylate (**II**) or styrene (**IV**), 1.265 g (12.5 mmol) of triethylamine, 0.105 g (0.4 mmol) of triphenylphosphine, and 0.0225 g (0.1 mmol) of palladium(II) acetate. The ampule was purged with argon, sealed, and placed into a reactor charged with isooctane and equipped with a reflux condenser. The reactor was subjected to microwave irradiation at a power of 140 W over a period of 10 min. When the substrate conver-

sion was complete, the ampule was cooled to room temperature and opened, 5 ml of water and 5 ml of chloroform were added, and the mixture was transferred to a separatory funnel. The organic phase was separated, the aqueous phase was extracted with chloroform (3×5 ml), and the extracts were combined with the organic phase, dried over Na_2SO_4, and concentrated. The product was isolated by column chromatography on neutral silica gel L 40/100 using hexane–diethyl ether (5:1) as eluent.

Methyl (2*E*)-3-(4-acetylphenyl)prop-2-enoate (III). Yield 1.753 g (86%), mp 107–108°C. IR spectrum, ν, cm^{-1}: 3069, 3024, 2949, 2928, 2916, 2853, 1715 (C=O, ester), 1672 (C=O, ketone), 1636 (C=C), 1603, 1456, 1439, 1412, 1362, 1329, 1265, 1200, 1177, 1007, 966, 849, 827. ^{1}H NMR spectrum, δ, ppm: 2.58 s (3H, CH_3CO), 3.78 s (3H, CH_3O), 6.49 d (1H, =CHCO, J = 16.2 Hz), 7.57 d (2H, H_{arom}, J = 8.3 Hz), 7.67 d (1H, =C**H**C_6H_4, J = 16.2 Hz), 7.93 d (2H, H_{arom}, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.59 (CH_3CO), 51.80 (OCH_3), 120.21 (=**C**HCOO), 128.05 (2C, C_{arom}), 128.76 (2C, C_{arom}), 137.92 (C_{arom}), 138.58 (C_{arom}), 143.18 (=**C**HC_6H_4), 166.81 (**C**$OOCH_3$), 197.21 (CH_3**C**O). Mass spectrum, m/z (I_{rel}, %): 204 (27) $[M]^+$, 190 (11), 189 (100) $[M - CH_3]^+$, 173 (7) $[M - CH_3O]^+$, 161 (13) $[M - CH_3CO]^+$, 131 (11), 102 (25), 76 (11).

1-{4-[(*E*)-2-Phenylvinyl]phenyl}ethan-1-one (V). Yield 1.761 g (79%), mp 146–148°C. IR spectrum, ν, cm^{-1}: 3080, 3044, 3019, 2951, 2924, 2853, 1678 (C=O), 1601, 1450, 1360, 1267, 964, 822, 754, 691. ^{1}H NMR spectrum, δ, ppm: 2.60 s (3H, CH_3CO), 7.12 d and 7.23 d (1H each, CH=CH, J = 16.3 Hz), 7.29–7.40 m (3H, H_{arom}), 7.52–7.60 m (4H, H_{arom}), 7.95 d (2H, H_{arom}, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.58 (CH_3CO), 126.48 (2C, C_{arom}), 126.80 (2C, C_{arom}), 127.43 (CH=), 128.30 (C_{arom}), 128.79 (2C, C_{arom}), 128.88 (2C, C_{arom}), 131.44 (CH=), 135.93 (C_{arom}), 136.68 (C_{arom}), 141.99 (C_{arom}), 197.48 (CH_3CO). Mass spectrum, m/z (I_{rel}, %): 223 (19) $[M + 1]^+$, 222 (85) $[M]^+$, 207 (100) $[M - CH_3]^+$, 179 (35), 178 (56), 152 (12), 89 (22).

Microwave-assisted reactions were performed using a Microdigest M 301 single mode microwave furnace (operating frequency 2450 MHz). The IR spectra were recorded from samples dispersed in mineral oil on a Shimadzu Prestige-21 spectrometer with Fourier transform. The ^{1}H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Bruker AM-300 instrument at 300 and 75.47 MHz, respectively, using tetramethylsilane as internal reference. Gas chromatographic–mass spectrometric analysis was performed using a Khromatek Kristall 5000 instrument coupled with a Finnigan DSQ mass-selective detector (electron impact, 70 eV).

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