Monatshefte für Chemie 131, 945–948 (2000)

Monatshefte für Chemie
Chemical Monthly

Zeolite HY and Silica Gel as New and Efficient Heterogenous Catalysts for the Synthesis of Triarylimidazoles under Microwave Irradiation

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Summary. Zeolite HY and silica gel efficiently catalyzed the three component condensation of benzil, benzaldehyde derivatives, and ammonium acetate under solvent-free conditions and microwave irradiation.

Keywords. Cyclocondensation; Microwave irradiation; Silica gel; Solvent-free condition; Triarylimidazole derivatives.

Introduction

Triarylimidazoles are used in photography as photosensitive compounds [1]. In addition, they are of interest because of their herbicidal [2], fungicidal [3], antiinflammatory [4], and antithrombotic [5] activities. There are many methods for the synthesis of imidazole derivatives based on transformations of oxazole, isoxazole, oxadiazole, pyrazole, and oxirane skeletons [6]. A general method for the synthesis of triarylimidazoles is the cyclocondensation of benzil, aldehydes, and ammonia or ammonium acetate in HOAc as the solvent under reflux and an N_2 atmosphere [7]. The application of microwaves in chemistry has now become an area of interest for the synthesis of a wide variety of compounds and efficient functional group transformation under solvent-free conditions [8].

In connection with our interest in the use of microwaves [9] for accelerating organic reactions and the biological importance of triarylimidazole derivatives, we report the synthesis of triarylimidazole derivatives **4a**–**h** under solvent-free conditions and microwave irradiation.

Results and Discussion

Zeolite HY is an acidic and efficient catalyst in organic synthesis [10]. The three component condensation of benzil, benzaldehyde derivatives **2a**–**h**, and

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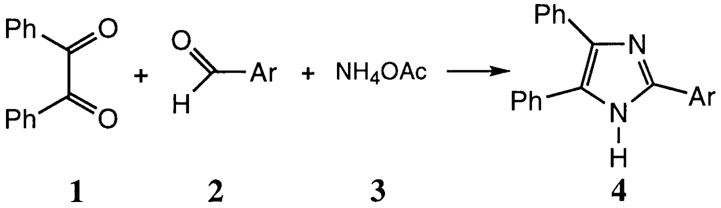

Scheme 1

Table 1. Solvent-free synthesis of imidazoles **4a–h** under microwave irradiation[a]

	Ar	Yield/%[b]	
		Zeolite HY	Silica gel
4a	C_6H_5	81	68
4b	4-$CH_3C_6H_4$	87	65
4c	4-$CH_3OC_6H_4$	92	68
4d	4-$NO_2C_6H_4$	94	89
4e	4-ClC_6H_4	85	65
4f	2-HOC_6H_4	80	62
4g	2,6-$Cl_2C_6H_3$	91	88
4h	4-$(CH_3)_2NC_6H_4$	80	54

[a] In all experiments, the reaction time was 6 min;

[b] all reported yields refer to isolated products

ammonium acetate catalyzed by zeolite HY and silica gel under solvent-free conditions and microwave irradiation was carried out according to Scheme 1 and Table 1.

In the classic approach [7], this cyclocondensation requires long reaction times (1.5–10 h) and refluxing in HOAc under an inert atmosphere. In addition, this method suffers from tedious and time-consuming work-up. In contrast, under solvent-free conditions, the reactions are completed within only 6 minutes and afford the products in high yields. Comparing the results shown in Table 1, we note that the best yields were achieved with zeolite HY (80–94%) which is comparable to the classic method. The products were characterized on the basis of their IR and ^1H NMR spectroscopic data and melting points. In the IR spectra the absence of the carbonyl and aldehyde absorption bonds are in accordance with the structure of reaction products. Absorption at 1585 cm^{-1} due to the C=N group was observed instead.

It is worth mentioning that in the absence of zeolite HY or silica gel under microwave irradiation the yield of the reactions were low and the reactants and products adhered to the reaction vessel walls which reduced reaction yields and sometimes lead to irreproducible results. In the cyclocondensation with anisaldehyde in HOAc without zeolite HY or silica gel under microwave irradiation, the yield was about 90%, but this procedure resulted in a difficult work-up in contrast to our solvent-free method.

In conclusion, we developed a general and rapid method for the synthesis of triarylimidazole derivatives which is characterized by simple set-up and work-up, high yields, low reaction times, and environmental advantages.

Experimental

Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-408 spectrometer as KBr disks. ^{1}H NMR spectra were determined in $CDCl_3$ with *TMS* as internal reference on an 80 MHz FT-NMR spectrometer (Bruker). A domestic microwave oven (Moulinex 2735 A) at 2450 MHz (100% power, 850 W) was used in all experiments.

General procedure

841 mg Benzil (4 mmol), 4 mmol aldehyde, 617 mg ammonium acetate (8 mmol), and 4 g silica gel or zeolite HY (prepared from zeolite NH_4Y in an oven at 600 °C for 5 h that afforded zeolite HY) were mixed thoroughly in a mortar. Then the reaction mixture was transferred into a beaker (250 cm^3) and irradiated with microwaves for 6 minutes. The progress of reaction was monitored by TLC using CH_2Cl_2:EtOAc = 90:10 as the eluent. The mixture was extracted with CH_2Cl_2 ($3\times30\,cm^3$), filtered, and washed with H_2O. The organic phase was removed by means of a rotary evaporator. Further purification by column chromatography (eluent CH_2Cl_2:EtOAc = 98:2) on silica gel gave the desired products.

2,4,5-Triphenyl-1H-imidazole (**4a**; $C_{21}H_{16}N_2$)

M.p.: 276–277 °C ([7a]: 275 °C); IR (KBr): $\nu = 3450$ (N–H), 3050 (C–H), 1600 (C=C), 1580 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.15$–8.00 (m, 15H, Ph), 9.20 (br s, NH) ppm.

2-(4-Methylphenyl)-4,5-diphenyl-1H-imidazole (**4b**; $C_{22}H_{18}N_2$)

M.p.: 231–232 °C ([7e]: 237–237.5 °C); IR (KBr): $\nu = 3450$ (N–H), 1600 (C=C), 1585 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.30$ (s, CH_3), 7.10–7.60 (m, 10H, Ph), 7.70 (d, 2H, $J = 10$ Hz, Ar), 7.30 (d, 2H, $J = 10$ Hz, Ar) ppm.

2-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazole (**4c**; $C_{22}H_{18}N_2O$)

M.p.: 227–228 °C ([7b]: 229 °C); IR (KBr): $\nu = 3450$ (N–H), 1610 (C=C), 1575 (C=N), 1385 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 3.90$ (s, OCH_3), 7.05 (d, 2H, $J = 8.8$ Hz, Ar), 7.30–7.80 (m, 10H, Ph), 7.90 (d, 2H, $J = 8.8$ Hz, Ar) ppm.

2-(4-Nitrophenyl)-4,5-diphenyl-1H-imidazole (**4d**; $C_{21}H_{15}N_3O_2$)

M.p.: 236–237 °C ([7b]: 240 °C); IR (KBr): $\nu = 3400$ (N–H), 1580 (C=N), 1515 (NO_2), 1335 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.15$–7.70 (m, 10H, Ph), 7.90–8.25 (AB, 4H, $J = 9$ Hz, Ar) ppm.

2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (**4e**; $C_{21}H_{15}ClN$)

M.p.: 261–263 °C ([7e]: 266–268 °C); IR (KBr): $\nu = 3450$ (N–H), 1600 (C=C), 1580 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.10$–7.60 (m, 10H, Ph), 7.35 (d, 2H, $J = 10$ Hz, Ar), 7.85 (d, 2H, $J = 10$ Hz, Ar) ppm.

2-(2-Hydroxyphenyl)-4,5-diphenyl-1H-imidazole (**4f**; $C_{21}H_{16}N_2O$)

M.p.: 208–209 °C ([7b]: 209 °C); IR (KBr): $\nu = 3200$ (O–H), 3050 (C–H), 1600 (C=C), 1580 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 6.70$–7.60 (m, 14H, Ar), 9.50 (br s, NH) ppm.

2-(2,6-Dichlorophenyl)-4,5-diphenyl-1H-imidazole (**4g**; $C_{21}H_{14}Cl_2N_2$)

M.p.: 237–238 °C ([7e]: 239–240 °C); IR (KBr): $\nu = 3400$ (N–H), 3050 (C–H), 1600 (C=C), 1580 (C=N), 1070 (C–Cl) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.00$–7.60 (m, 13H, Ar), 9.70 (br s, NH) ppm.

2-(4-Dimethylaminophenyl)-4,5-diphenyl-1H-imidazole (**4h**; $C_{23}H_{21}N_3$)

M.p.: 257–258 °C ([7e]: 259.5–260 °C); IR (KBr): $\nu = 3050$ (C–H), 2850 (C–H), 1615 (C=C), 1600 (C=N), 1360 (C–N) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.90$ (s, $2CH_3$), 6.60 (d, 2H, $J = 8.9$ Hz, Ar), 7.10–7.60 (m, 10H, Ph), 7.70 (d, 2H, $J = 8.9$ Hz, Ar) ppm.

Acknowledgements

We are grateful to Prof. *J. Ipaktschi* for a generous gift of zeolite NH_4Y.

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Received February 22, 2000. Accepted (revised) March 22, 2000