HETEROCYCLES, Vol. 63, No. 1, 2004, pp. 87 - 93
Received, 28th August, 2003, Accepted, 22nd October, 2003, Published online, 31st October, 2003

# ONE-POT SYNTHESIS OF TETRA-SUBSTITUTED IMIDAZOLES ON SILICA GEL UNDER MICROWAVE IRRADIATION

Yu Xu, Yan-Zhi liu, Lei Rui, Lei Liu, and Qing-Xiang Guo*

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China (e-mail: qxguo@ustc.edu.cn )

Abstract– A new procedure for synthesis of tetra-substituted imidazoles was developed. A series of imidazole derivatives including six new compounds were synthesized by this procedure *via* condensation of benzoin, aromatic aldehyde, amine and ammonium acetate in the presence of silica gel under solvent-free microwave irradiation.

## INTRODUCTION

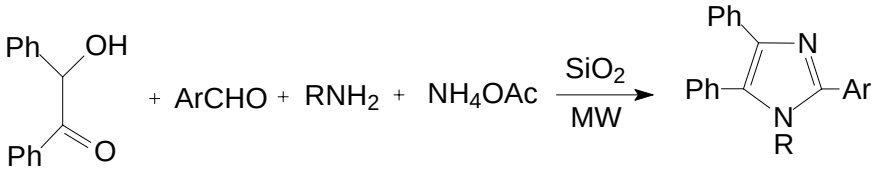
Imidazole nucleus is the main component of some important biological molecules, such as histidine, Vitamin B12, purines, histamine and biotin. It also presents in many natural and synthetic drug molecules, for example, cimetidine, azomycin and metronidazole.[1] Compounds with imidazole ring systems have many pharmaceutical activities and play important roles in biochemical processes.[2]

Because imidazoles are versatile intermediates in the manufacture of pharmacologically active compounds,[3] many methods have been developed for the synthesis of substituted imidazoles. Typical methods include: condensation of diones, aldehydes, primary amines, and ammonia;[4] condensation of benzoin or benzoin acetate with aldehydes, primary amines and ammonia in the presence of copper acetate;[5] four-component condensations of diones, aldehydes, primary amines, and ammonia acetate in acetic acid under reflux conditions;[6] cyclization of sulfonamides with mesoionic 1,3-oxazolium-5-olates;[7] condensation of β-carbonyl-*N*-acyl-*N*-alkylamines with ammonium acetate in refluxing HOAc;[8] and conversion of *N*-(2-oxo)amides with ammonium triflouroacetate under neutral conditions;[9] iron and copper catalyzed reaction of benzylamine with carbon tetrachloride.[10]

Recently, microwave-assisted synthesis in organic chemistry is quickly growing.[11] Many organic reactions proceed much faster and get higher yields under microwave irradiation compared to conventional heating. Supported reagents on solid surface have been widely employed in organic synthesis. Reagents impregnanted on solid materials present advantages over the conventional solution

phase reactions, for the good dispersion of active sites leading to improved reactivity and milder reaction conditions. A solvent-free reaction with microwave irradiation would reduce reaction time, and provide easier work-up procedures. In contrast to the traditional application of solid phase in synthesis, microwave technology does not involve the solid phase linking with the reactants and cleaving with the products. The recycling of the inorganic solid support makes the procedure more environmentally benign. Two research groups have recently reported a one-pot condensation of benzil, aldehyde, amine and ammonium acetate on alumina or silica solid support under microwave irradiation.[3, 12] It was found that microwave irradiation and solid support in the solventless reaction considerably shortened the reaction time and greatly reduced waste production.[13]

In our laboratory, some imidazole derivatives have been synthesized with microwave assistance.[14] It was interesting to find that use of benzoin instead of benzil as starting material in the condensation also produced the desired products efficiently (Scheme 1). To our knowledge, the benzils are usually prepared from benzoins catalyzed by various toxic oxidants, such as thallium nitrate, ytterbium(III) nitrate, ammonium nitrate-copper acetate, clayfen, ammonium chlorochromate-alumina, nickel acetate, iron(III) chloride and bismuth(III) nitrate-copper(II) acetate.[15] Obviously, direct use benzoin rather than benzil in the synthesis of imidazoles represents a significant improvement in the syntheses toward to greener chemistry.




Scheme 1

## RESULTS AND DISCUSSION

Tetra-substituted imidazoles were synthesized under microwave irradiation in good yield (Table 1). In order to avoiding overheating, two 10-minute irradiations were performed. All products, six of them (**b**, **c**, **e**, **f**, **g**, **o**) were firstly synthesized, were characterized by melting points, and elemental analyses, IR, MS, $^{1}$H NMR and $^{13}$C NMR spectroscopies.

From Table 1, it can be seen that this procedure could be applied to a broad range of substituted aromatic and aliphatic amines and aromatic aldehydes. The results indicated that good yields were obtained when the *p*-methoxy- and *p*-methylbenzaldehyde were used as starting materials (Entries a, c, l, n), however, when *p*-dimethylaminobenzaldehyde was used, the yield is not so good (Entry o), but still acceptable. Interestingly, it was found that benzoin could be used in the condensation yielding imidazole in absence of any oxidizing reagent. A control experiment of the condensation of benzoin, aldehyde, amine and

ammonium acetate under conventional acetic acid reflux conditions was run, no corresponding imidazole was isolated from the reaction mixture. It was in agreement with the previous finding that an oxidizing reagent such as Cu(II) was needed in the conventional condensation.[5] This finding demonstrated that the microwave irradiation and silica gel support would play important roles in the reaction.

Table 1. Microwave-assisted synthesis of tetra-substituted imidazoles on silica gel

| Entry | Ar | R | Yield (%) / Time(min) | |
|---|---|---|---|---|
| | | | This study | Literature[ref] |
| a | *p*-$CH_3O$-$C_6H_4$ | $PhCH_2$ | 91 / 10×2* | 87 / 180 [1] |
| b | | $PhCH_2CH_2$ | 87 / 10×2 | - |
| c | | cyclohexyl | 95 / 10×2 | - |
| d | *p*-HO-$C_6H_4$ | $PhCH_2$ | 71 / 10×2 | 43 / 180 [1] |
| e | | $PhCH_2CH_2$ | 65 / 10×2 | - |
| f | | cyclohexyl | 61 / 10×2 | - |
| g | | Ph | 60 / 10×2 | - |
| h | $C_6H_5$ | $PhCH_2$ | 86 / 10×2 | 87 / 6 [3] |
| i | | $PhCH_2CH_2$ | 80 / 10×2 | 80 / 20 [12] |
| j | | cyclohexyl | 89 / 10×2 | 80 / 6 [3] |
| k | | Ph | 75 / 10×2 | 79 / 6 [3] |
| l | *p*-Me-$C_6H_4$ | $PhCH_2$ | 90 / 10×2 | 90 / 6 [3] |
| m | | $PhCH_2CH_2$ | 83 / 10×2 | 68 / 20 [12] |
| n | | cyclohexyl | 92 / 10×2 | 87 / 6 [3] |
| o | *p*-$(CH_3)_2N$-$C_6H_4$ | *m*-$NO_2$-$C_6H_4$ | 50 / 10×2 | - |

*Irradiation for two 10 min intervals with cooling to room temperature between intervals .

Interestingly, it was reported recently by Balalaie *et al.*[16] that benzoins were oxidized on zeolite A using microwave irradiation under solvent-free conditions, in which air functioned as oxidant in the conversion. It was proposed that the zeolite A was significant in the Balalaie's benzoin oxidation. In our study the simple silica gel was adequate for a rapid and clean oxidation of the condensation mixture to imidazole, although at the present stage we cannot conclude whether benzoin is oxidized before condensation or after partially condensation.

In spite of the fact that one more chemical transformation, such as oxidation has to be involved in the condensation to imidazole, the yields of the reaction reported herein are as good as those previously reported (See Table 1).[3, 12] Usyatinsky and Khmelnitsky[12] reported that a small amount of acetic acid was needed to accelerate the condensation, however, in our work the acetic acid was not necessary.

Based on the results described above, we can conclude that a facile and environmentally benign one-pot synthesis of tetra-substituted imidazole derivatives from benzoin, aldehydes, amines and ammonium acetate was developed.

**EXPERIMENTAL**

All reported yields are isolated yields after column chromatography. MS spectra were run on a GCT-CA064 spectrograph. All melting points are uncorrected and were measured on WRS-1A melting point apparatus. IR spectra were run on a Bruker spectrophotometer and expressed in $cm^{-1}$(KBr). $^{1}$HNMR and $^{13}$CNMR spectra were recorded on FT-NMR Bruker AV-400 (400 MHz) or Bruker AV-300 (300 MHz) in DMSO-$d_6$ with TMS as internal reference. Elemental analysis was performed by the Elementar Vario EL-III. All the reactions were conducted in a commercial microwave oven. (Galanz WD800B, 2450 Hz, output power 800 W)

Typical procedure for the synthesis of tetra-substituted imidazoles as follows: A mixture of silica gel (15.4 g) and ammonium acetate (7.7 g, 100 mmol) was ground fully. A solution of benzoin (1.06 g, 5 mmol), aldehyde (5 mmol) and amine (5 mmol) in 20 mL of ethyl acetate was added to the mixture and mixed thoroughly. The solvent was allowed to evaporate under reduced pressure and the dry residue was irradiated at 160W (20% power) at 120℃ in 10 min. The mixture was cooled, stirred and irradiated for another 10 min. The mixture was cooled to rt and extracted with ethyl acetate (3×50 mL). The combined organic solution was filtered and the solvent was evaporated by a rotary evaporator. The product was purified by column chromatography.

1-Benzyl-2-(4-methoxylphenyl)-4,5-diphenylimidazole (**1a)**: MS m/z: $(M+H)^+$ 417.1964 (Calcd 417.1967); mp 158-159℃ (ethyl acetate); lit.,[1] 153-155℃; IR(KBr) ν 2967(C-H), 1609(C=C), 1575(C=N), 1500, 1450 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz) $\delta_H$: 3.79 (s, 3H, $CH_3$), 5.14 (s, 2H, $CH_2$), 6.76-7.60 (m, 19H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 75 MHz) $\delta_C$: 47.6, 55.2, 114.0, 123.1, 125.6, 126.1, 126.2, 127.2, 128.1, 128.5, 128.8, 128.9, 129.8, 129.9, 130.7, 130.8, 134.6, 136.6, 137.4, 147.0, 159.6.

2-(4-Methoxylphenyl)-1-phenethyl-4,5-diphenylimidazole (**1b)**: MS m/z: $(M+H)^+$ 431.2128 (Calcd 431.2123); mp126-127℃ (ethyl acetate); IR(KBr) ν 2958(C-H), 1610(C=C), 1575(C=N), 1498, 1459 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 2.53 (t, 2H, J=7.5 Hz , $CH_2$), 3.84 (s, 3H, $CH_3$), 4.05 (t, 2H, J=7.5 Hz , $CH_2$), 6.68-7.60 (m, 19H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 75 MHz), $\delta_C$: 35.6, 45.8, 55.2, 114.0, 123.5, 126.0, 126.5, 127.9, 128.2, 128.4, 128.8, 129.0, 129.3, 130.0, 130.9, 131.1, 134.7, 136.2, 137.3, 146.6, 159.5; Anal. Calcd for $C_{30}H_{26}N_2O$: C 83.68, H 6.09, N 6.51. Found C 83.56, H 5.89, N 6.41.

1-Cyclohexyl-2-(4-methoxyphenyl)-4,5-diphenylimidazole (**1c)**: MS m/z: $(M+H)^+$ 409.2282 (Calcd 409.2280); mp 191-193℃ (ethyl acetate); IR(KBr) ν 2937(C-H), 1612(C=C), 1541(C=N), 1493, 1443 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 0.55-1.99 (m, 10H, $CH_2$), 3.84 (s, 3H, $CH_3$), 4.00-4.04 (m, 1H, CH), 7.03-8.03 (m, 14H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 75 MHz), $\delta_C$: 14.1, 20.8, 55.2, 59.8, 113.8, 114.1, 123.1, 125.9, 126.7, 127.9, 128.4, 128.8, 129.1, 131.0, 132.1, 145.6, 159.4.

1-Benzyl-2-(4-hydroxyphenyl)-4,5-diphenylimidazole (**1d)**: MS m/z: $(M+H)^+$ 403.1812 (Calcd 403.1810); mp 258-259℃ (ethyl acetate); lit.,[1] 134-135℃; IR(KBr) ν 2934(C-H), 1611(C=C),

1543(C=N), 1482, 1451 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 5.12 (s, 2H, $CH_2$), 6.76 -7.46 (m, 19H, Ar), 9.79 (s, 1H, OH); $^{13}$C-NMR (DMSO-$d_6$, 75 MHz) $\delta_C$ 47.6, 115.3, 121.5, 125.6, 126.0, 127.1, 128.1, 128.5, 128.8, 128.9, 129.6, 130.0, 130.8, 134.7, 136.5, 137.5, 147.5, 158.0.

2-(4-Hydroxyphenyl)-1-phenethyl-4,5-diphenylimidazole (**1e)**: MS m/z: $(M+H)^+$ 417.1970 (Calcd 417.1967); mp 238-239℃ (ethyl acetate); IR(KBr) ν 2922(C-H), 1614(C=C), 1542(C=N), 1485, 1443 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz ), $\delta_H$: 1.99 (t, 2H, J=7.5 Hz, $CH_2$), 4.02 (t, 2H, J=7.5 Hz, $CH_2$), 6.42 -7.88 (m, 19H, Ar), 9.79 (s, 1H, OH); $^{13}$C-NMR (DMSO-$d_6$, 75 MHz), $\delta_C$: 35.6, 45.8, 115.4, 121.9, 126.0, 126.5, 128.0, 128.3, 128.4, 128.8, 129.1, 130.2, 130.9, 131.2, 134.8, 136.0, 137.5, 147.1, 157.9; Anal. Calcd for $C_{29}H_{24}N_2O$: C 83.62, H 5.81, N 6.73. Found C 83.55, H 5.73, N 6.55.

1-Cyclohexyl-2-(4-hydroxyphenyl)-4,5-diphenylimidazole (**1f)**: MS m/z: $(M+H)^+$ 395.2122 (Calcd 395.2123); mp 249-251℃ (ethyl acetate); IR(KBr) ν 2934 (C-H), 1609 (C=C), 1542 (C=N), 1494, 1458 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 0.57-1.99 (m, 10H, $CH_2$), 3.99-4.04 (m, 1H, CH), 6.82-7.53 (m, 14H, Ar), 9.81 (s, 1H, OH); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 14.0, 20.7, 59.7, 115.4, 121.6, 126.3, 126.8, 127.0, 127.3, 127.5, 128.0, 128.3, 128.5, 131.3, 135.4, 136.6, 146.0, 157.8.

2-(4-Hydroxyphenyl)-1,4,5-triphenylimidazole (**1g)**: MS m/z: $(M+H)^+$ 389.1660 (Calcd 389.1654); mp 218-220℃ (ethyl acetate); IR(KBr) ν 1608(C=C), 1533(C=N), 1496, 1460 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 6.64-7.48 (m, 19H, Ar), 9.69 (s, 1H, OH); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 114.8, 126.3, 128.0, 128.2, 128.3, 128.5, 128.7, 129.0, 129.7, 130.4, 130.5, 131.0, 136.7, 146.3, 157.6.

1-Benzyl-2,4,5-triphenylimidazole (**1h)**: MS m/z: $(M+H)^+$ 387.1885 (Calcd 387.1861); mp 165-167℃ (ethyl acetate); lit.,[3] 163-164℃; IR(KBr) ν 3037(C-H), 1602(C=C), 1498(C=N), 1480, 1449 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 5.16 (s, 2H, $CH_2$), 6.74-7.66 (m, 20H, Ph); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 47.6, 125.5, 126.0, 126.2, 127.1, 128.0, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 130.1, 130.5, 130.7, 130.8, 134.4, 136.8, 137.2, 147.0; Anal. Calcd for $C_{28}H_{22}N_2$: C 87.01, H 5.74, N 7.25. Found C 87.04, H 5.70, N 7.09.

1-Phenethyl-2,4,5-triphenylimidazole (**1i)**: MS m/z: $(M+H)^+$ 401.2014 (Calcd 401.2018); mp 161-163℃ (ethyl acetate); IR(KBr) ν 2960 (C-H), 1601(C=C), 1498(C=N), 1480, 1444 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 2.50-2.56 (t, 2H, J=9.0 Hz, $CH_2$), 4.02-4.08 (t, 2H, J=9.0 Hz, $CH_2$), 6.67-7.67 (m, 20H, Ph); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 35.5, 45.8, 125.1, 125.9, 126.0, 126.4, 127.9, 128.2, 128.3, 128.5, 2×128.6, 128.7, 128.8, 129.0, 130.8, 130.9, 131.1, 134.5, 137.2, 146.6; Anal. Calcd for $C_{29}H_{24}N_2$: C 86.96, H 6.04, N 7.00. Found C 86.67, H 5.94, N 6.95.

1-Cyclohexyl-2,4,5-triphenylimidazole (**1j)**: MS m/z: $M^+$ 378.2086 (Calcd 378.2096); mp 168-170℃ (ethyl acetate); lit.,[3] 167-169℃; IR(KBr) ν 2932 (C-H), 1640(C=C), 1558(C=N), 1503, 1445 $cm^{-1}$; $^{1}$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 0.50-1.87 (m, 10H, $CH_2$), 4.37 (m, 1H, CH), 6.75-8.10 (m, 15H, Ph).

1,2,4,5-Tetraphenylimidazole (**1k):** MS m/z: $(M+H)^+$ 373.1709 (Calcd 373.1705); mp 216-218℃ (ethyl acetate); lit.,[3] 216-218℃; IR(KBr) ν 1600(C=C), 1497(C=N), 1480, 1443 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 6.80-7.64 (m, 20H, Ph); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 126.2, 126.3, 128.0, 128.1, 128.3, 128.6, 129.0, 130.3, 131.0, 131.2, 134.3, 136.6, 136.7, 145.9; Anal. Calcd for $C_{27}H_{20}N_2$: C 87.06, H 5.42, N 7.53. Found C 86.87, H 5.37, N 7.24.

1-Benzyl-2-(4-methylphenyl)-4,5-diphenylimidazole (**1l):** MS m/z: $(M+H)^+$ 401.2040 (Calcd 401.2018); mp 158-160℃ (ethyl acetate); lit.,[3] 163-166℃; IR(KBr) ν 2926(C-H), 1601(C=C), 1498(C=N), 1484, 1452 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 2.33 (s, 3H, $CH_3$), 5.15 (s, 2H, $CH_2$), 6.74-7.66 (m, 19H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 20.7, 47.5, 125.5, 126.0, 126.1, 127.1, 127.8, 128.0, 128.3, 128.4, 128.7, 128.8, 129.0, 129.9, 130.5, 130.7, 134.5, 136.7, 137.3, 138.2, 147.1; Anal. Calcd for $C_{29}H_{24}N_2$: C 86.96, H 6.04, N 7.00. Found C 86.70, H 5.90, N 6.80.

2-(4-Methylphenyl)-1-phenethyl-4,5-diphenylimidazole (**1m):** MS m/z: $(M+H)^+$ 415.2173 (Calcd 415.2174); mp 124-125℃ (ethyl acetate); IR(KBr) ν 2921(C-H), 1602(C=C), 1500(C=N), 1482, 1451 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 2.40 (s, 3H, $CH_3$), 2.54 (t, 2H, J= 9.0 Hz, $CH_2$), 4.07 (t, 2H, J= 9.0 Hz, $CH_2$), 6.68-7.58 (m, 19H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 20.9, 35.6, 45.8, 126.0, 126.5, 128.0, 128.2, 128.3, 128.4, 128.5, 128.8, 129.0, 129.1, 129.5, 130.9, 131.0, 134.7, 136.3, 137.3, 138.2, 146.7; Anal. Calcd for $C_{30}H_{26}N_2$: C 86.91, H 6.33, N 6.76. Found C 86.68, H 6.25, N 6.60.

1-Cyclohexyl-2-(4-methylphenyl)-4,5-diphenylimidazole (**1n):** MS m/z: $(M+H)^+$ 393.2356 (Calcd 393.2331); mp 162-164℃ (ethyl acetate); lit.,[3] 162-164℃; IR(KBr) ν 2929(C-H), 1629 (C=C), 1550 (C=N), 1494, 1450 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 0.55-1.99 (m, 10H, $CH_2$), 2.35 (s, 3H, $CH_3$), 3.47 (m, 1H, CH), 6.54-7.98 (m, 14H, Ar).

2-(4-Dimethylaminophenyl)-1-(3-nitrophenyl)-4,5-diphenylimidazole (**1o):** MS m/z: $M^+$ 460.1929 (Calcd 460.1899); mp 238-240℃ (ethyl acetate); lit.,[3] 167-169℃; IR(KBr) ν 2923(C-H), 1616(C=C), 1551(C=N), 1508, 1497 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$, 300 MHz), $\delta_H$: 2.97 (s, 6H, $CH_3$), 6.78 -7.92 (m, 18H, Ar); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz), $\delta_C$: 111.8, 118.3, 121.5, 126.2, 126.9, 127.1, 127.3, 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 129.4, 129.5, 135.5, 141.7, 146.4, 150.2.

**ACKNOWLEDGEMENTS**

This research was supported by the Chinese Academy of Sciences, State Ministry of Science and Technology, and University of Science and Technology of China.

**REFERENCES**

1. U. Ucucu, N. G. Karaburun, and I. Isikdag, *Farmaco*, 2001, **56**, 285.

2. J. G. Lombardino and E. H. Wiseman, *J. Med. Chem.*, 1974, **17**, 1182.
3. S. Balalaie and A. Arabanian, *Green Chem.*, 2000, **2**, 274.
4. V. Stoeck and W. Schunack, *Arch. Pharm.,* 1974, **307**, 922.
5. V. Stoeck and W. Schunack, *Arch. Pharm.,* 1976, **309**, 421; B. H. Lipshutz and M. C. Morey, *J. Org. Chem.,* 1983, **48**, 3745.
6. H. Schubert and H. Stodolka, *J. Prakt. Chem.,* 1963, **22**, 130; B. Krieg and G. Z. Manecke, *Naturforschung*, 1967, **22b**, 132.
7. R. Consonni, P. D. Croce, R. Ferraccioli, and C. L. Rosa, *J. Chem. Res. (S),* 1991, 188.
8. D. A. Evans and K. M. Lundy, *J. Am. Chem. Soc.*, 1992, **114**, 1495; P. Schneiders, J. Heinze, and H. Baumgartel, *Chem. Ber.*, 1973, **106**, 2415.
9. C. F. Claiborne, N. J. Liverton, and K. T. Nguyen, *Tetrahedron Lett.*, 1998, **39**, 8939.
10. J. Tsuji, K. Sakai, H. Nemoto, and H. Nagashima, *J. Mol. Catal.,* 1983, **18**, 169.
11. S. Caddick, *Tetrahedron*, 1995, **51**, 10403; C. R. Strauss and R. W. Trainor, *Aust. J. Chem.*, 1995, **48**, 1665; S. Deshayes, M. Liagre, A. Loupy, J. L. Luche, and A. Petit, *Tetrahedron*, 1999, **55**, 10851; R. S. Varma, *Green Chem.*, 1999, **1**, 43; P. Lidstrom, J. Tierney, B. Wathey, and J. Westman, *Tetrahedron*, 2001, **57**, 9225.
12. A. Y. Usyatinsky and Y. L. Khmelnitsky, *Tetrahedron Lett.,* 2000, **41**, 5031.
13. D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1; M.-W. Lu, W.-X. Hu, and L.-H. Yun, *Chin. J. Org. Chem.*, 1995, **15**, 561; A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, and D. Mathe, *Synthesis*, 1998, 1213; N. Elander, J. R. Jones, S.-Y. Lu, and S. Stone-Elander, *Chem. Soc. Rev.*, 2000, **29**, 239; Y.-W. Sha, Y. Wang, J. Ge, and X. Wang, *Chin. J. Org. Chem.,* 2001, **21**, 102; J. Lu, B.-Q. Yang, Y.-J. Bai, and H.-R. Ma, *Chin. J. Org. Chem.,* 2001, **21**, 640; J. Wang and F.-C. Jiang, *Chin. J. Org. Chem.,* 2002, **22,** 212; G.-C. Yang, Z.-X.Chen, and C.-L. Hu, *Chin. J. Org. Chem.,* 2002, **22**, 289.
14. This is unpublished work.
15. A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron Lett.,* 1970, 5281; P. Girard and H. B. Kagan, *Tetrahedron Lett.,* 1975, 4513; G.-S. Zhang, Q.-Z. Shi, and K. Cai, *Chin. J. Org. Chem.*, 1998, **18**, 263; S. A. Tymonko, B. A. Nattier, and R. S. Mohan, *Tetrahedron Lett.,* 1999, **40**, 7657; Z.-B. Cai and Z.-G. Shi, *Chin. J. Org. Chem.*, 2002, **22**, 446.
16. S. Balalaie, M. Golizeh, and M. S. Hashtroudi, *Green Chem.*, 2000, **2**, 277.