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Michael Addition Of Indole With 1,5-Diaryl-1,4-Pentadien-3-Ones Catalyzed By p-Toluenesulfonic Acid (PTSA) Under Ultrasound

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ABSTRACT

The Michael addition of indole with 1,5-diaryl-1,4-pentadien-3-ones catalyzed by p-toluenesulfonic acid(PTSA) was carried out in excellent yields within 30-110 min in anhydrous ethanol under ultrasonic irradiation.

KEYWORDS

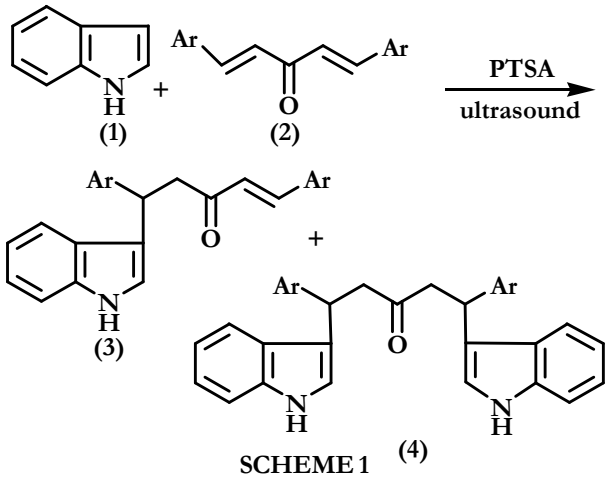
1,5-Diaryl-1,4-pentadien-3-one;
Michael addition;
Ultrasonic irradiation.

INTRODUCTION

Indoles and their derivatives are used as antibiotics in the field of pharmaceultieals[1]. Among various indole derivatives, 3-substituted indoles are important building blocks in the synthesis of natural products and in the design of therapeutic agents[2]. Therefore, a variety of methods have been reported for the preparation of this class of compounds[3]. A simple and direct method for the synthesis of 3-substituted indoles involves the conjugate addition of indoles to α, β–unsaturated compounds in the presence of either protic[4] or Lewis acid[5]. In 2003, β–indolylketones were found to be formed in acetonitrile in the presence of catalyst $Bi(OTf)_3$[6]. However, acetonitrile is not an environmentally-friendly solvent in the context of green chemistry. In the same year, Wang et. al. reported indole undergoes conjugate addition with α, β-nsaturated ketones by means of alkylation of indole in the presence of iodine at room temperature to afford the corresponding adducts in excellent yields. But the reaction time is very long to 4-12h[7].

PTSA is explored extensively in organic reactions and is a cheap and easy to obtain catalyst for a variety of reactions such as cyclodehydration[8], oxidative α-tosyloxylation[9], and protection of carbonyl group[10]. Recently, Ji reported that PTSA could promote efficiently the conjugate addition reaction of indoles with α, β-unsaturated ketone gave excellent yields within 1.5-4h[11].

Ultrasound has increasingly been used in organic synthesis in the last three decades. Compared with traditional methods, the procedure is more convenient and easily controlled. A large number of organic reactions can be carried out in higher yields, shorter reaction time or milder conditions under ultrasound irradiation[12]. So many literatures have been reported the Michael addition of indole to chalcones. However,



SCHEME 1

the conjugate addition of indole with 1,5-diaryl-1,4-pentadien-3-ones have been poorly documented. In continuation of our work in the synthesis of indole derivatives[13] we wish to report an efficient and practical Michael addition of indole to 1,5-diaryl-1,4-pentadien-3-ones catalyzed by PTSA under ultrasound irradiation(SCHEME 1).

EXPERIMENTAL

Apparatus and analysis

Liquid substrates were distilled prior to use. Melting points were uncorrected. ^{1}H-NMR spectra were measured on a Bruker AVANCE 400(400 MHz) spectrometer using TMS as the internal standard. MS were determined on a SHIMADZU GCMS-QP2010 spectrometer(EI, 10-200eV). Elemental analyses were measured on a HERAEUS(CHNO, Rapid) analyzer. Sonication was performed in Shanghai Branson-CQX ultrasonic cleaner(with a frequency of 25 kHz and a nominal power 250W) and SK 250 LH ultrasonic cleaner(with a frequency of 40 kHz, 59 kHz and a nominal power 250 W; Shanghai Kudos Ultrasonic Instrument Co., Ltd.). The reaction flask was located in the cleaner, where the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by addition or removal of water from ultrasonic bath.

General procedure

The preparation of 1,5-diaryl-1,4-pentadien-3-ones were referred to Ref.[14].Indole(1, 1.75mmol) and 1,5-diaryl-1,4-pentadien-3-ones(2, 1mmol) were dissolved in anhydrous ethanol(4mL) in a 50 mL conical flask. PTSA(2mmol) was then added and the mixture was irradiated in the water bath of an ultrasonic cleaner for the period as indicated in TABLE 1(sonication was continued until 1,5-diaryl-1,4-pentadien-3-ones disappeared by TLC). The mixture was extracted with ethyl acetate(3x15mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate for 12h and filtered. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was separated by column chromatography on silica(200-300 mesh). The authenticity of products were established by their ^{1}H NMR, MS or/and elemental analysis data.

TABLE 1 : Effect of reaction condition on Michael addition under ultrasonic irradiation

Entry	Molar ratio of 1/2/Cat.	Frequency, kHz	Time, min	Isolated yield, %	
				Overall	3/4
a	1:1:1	silent, stir.	30	55	43/12
b	1:1:1	25	30	72	61/11
c	1:1:1	40	30	68	57/11
d	1:1:1	59	30	62	54/8
e	1:1:1.5	25	30	75	63/12
f	1:1:2	25	30	82	65/17
g	1.5:1:2	25	30	84	50/34
h	1.75:1:2	25	30	98	35/63
i	2:1:2	25	30	97	30/67

3a solid, m.p

164-164.5°C. ^{1}H-NMR (DMSO): δ3.42 (dd, J=7.6, 16.0 Hz, 1H), 3.60(dd, J=7.6, 16.2 Hz, 1H), 4.83(t, J=7.6 Hz, 1H), 6.89-7.62(m, 17H), 10.86(s, 1H, NH) ppm. m/z (%): 351(43), 220(40), 206(100), 178(10), 131(13), 115(7), 103(33), 77(19). Anal.calcd.for $C_{25}H_{21}NO$: C, 85.47; H, 5.98; N, 3.99; found C, 85.48; H,5.99; N, 4.01.

4a solid, m.p

198-199 °C. ^{1}H NMR (DMSO): δ3.25(dd, J=7.6, 14.8 Hz, 2H), 3.33(dd, J=7.6, 14.8 Hz, 2H), 4.63 (t, J=7.2 Hz, 2H), 6.86-7.33(m, 20H), 10.81(s, 2H, NH) ppm. m/z(%): 468(34), 351(6), 262(26), 219 (25), 206(100), 178(14), 143(5), 130(23), 115(6), 103 (11),

77 (6). Anal. calcd. for $C_{33}H_{28}N_2O$: C, 84.61; H, 5.98; N, 5.98; found C, 84.62; H, 5.99; N, 6.00;

3b viscous liquid

^{1}H NMR (DMSO): δ2.80(s, 3H), 2.92(s, 3H), 3.28(dd, J=8.0, 16.4 Hz, 1H), 3.44(dd, J=8.0, 16.4 Hz, 1H), 4.68(t, J=7.6 Hz, 1H), 6.75-7.60(m, 15H), 10.80(s, 1H, NH) ppm. m/z (%): 414(83), 331(21), 287(40), 211(100), 198(4), 184(3), 156(19), 143 (56), 117(11), 121(10), 77(13), 44(23). Anal.calcd.for $C_{29}H_{31}N_3O$: C, 79.63; H, 7.09; N, 9.61; found C, 79.66; H, 7.16; N, 9.62.

4b viscous liquid

^{1}H-NMR (DMSO): δ2.80(s, 6H, CH_3), 3.05 (dd, J=8.0, 16.4 Hz, 2H), 3.11(dd, J=8.0, 16.4 Hz, 2H), 4.50(t, J=7.6 Hz, 2H), 6.69-7.33(m, 18H), 10.75 (s, 2H, NH) ppm. m/z (%):437(3),393(55), 317(17), 303(30), 291(3), 263(22), 249(25), 132(11), 117(3), 77(9), 44(98). Anal.calcd.for $C_{37}H_{38}N_4O$: C, 80.14; H, 6.86; N, 10.11; found C, 80.11; H,6.89; N, 10.13.

3c solid, m.p.

156-158 ^{0}C. ^{1}H-NMR (DMSO): δ 3.35(dd, J=7.6, 15.0 Hz, 1H), 3.51(dd, J=7.6, 15.8 Hz, 1H), 3.68 (s, 3H), 3.81(s, 3H), 4.78(t, J=7.6 Hz, 1H), 6.79-7.66 (m, 15H), 10.83(s, 1H, NH) ppm.m/z(%): 411(81), 249(22), 236(100), 221(5), 204(4), 178(3), 257(19), 133(56), 115(11), 103(10), 77(11). Anal.calcd.for $C_{27}H_{25}NO_3$: C 78.83, H, 6.08; N, 3.41; found C,78.85; H, 6.12; N,3.42.

4c solid, m.p

150-152 ^{0}C. ^{1}H NMR(DMSO): δ3.11(dd, J=8.0, 13.2 Hz, 2H), 3.19(dd, J=7.6, 12.6Hz, 2H), 3.68(s, 6H), 4.57-4.60(m, 2H), 6.72-7.33(m, 18H), 10.78(s, 2H, NH) ppm.m/z(%): 293(3), 236(55), 204(17), 192(30), 176(2), 165(22), 133(15), 117(10), 102 (2), 77(6), 43(57), 39(100). Anal.calcd.for $C_{34}H_{32}N_2O_3$: C 79.07, H, 6.20; N, 5.43; found C, 79.10; H,6.23; N, 5.46.

3d solid, m.p

150-152^{0}C. ^{1}H-NMR (DMSO): δ1.25(s, 3H), 2.18(s, 3H), 3.34(dd, J=7.6, 15.8Hz, 1H), 3.47(dd, J=7.6, 15.8 Hz, 1H), 4.90(t, J=7.6Hz, 1H), 6.77-7.70m, 15H), 10.83 (s, 1H, NH) ppm. m/z(%): 379 (98), 234(39), 220(100), 204(15), 178(8), 145(24), 130(8), 117(65), 102(4), 77(5). Anal.calcd.for $C_{27}H_{25}NO$: C 85.49, H, 6.60; N, 3.69; found C, 85.50; H, 6.63; N, 3.71.

4d solid, m.p

132-134^{0}C. ^{1}H NMR(DMSO): δ2.21(s, 6H), 3.11 (dd, J=7.6, 15.8Hz, 2H), 3.23(dd, J=7.6, 15.8 Hz, 2H), 4.57-4.62(q, 2H), 6.86-7.33(m, 18H), 10.79 (s, 2H, NH)ppm. m/z(%): 496(30), 379(18), 276 (41), 233(40), 220 (100), 204(21), 178(13), 143 (10), 130(38), 117(23), 77(5). Anal.calcd. for $C_{34}H_{32}N_2O$: C, 84.30; H, 6.61; N, 5.79; found C, 84.32; H, 6.63,; N, 5.82.

3e solid, m.p

69-71^{0}C. ^{1}H NMR(DMSO): δ3.66(dd, J=8.4, 16.4 Hz, 1H), 4.04(dd, J=8.4, 16.4Hz, 1H), 5.29(t, J=7.4 Hz, 1H), 7.03-7.84(m, 15H), 10.94(s, 1H, NH) ppm. m/z (%): 421(65), 419(96), 356(9), 254(72), 240(100), 218(15), 204(34), 189(5), 143(11), 137(43), 117(37), 101(67), 89(16), 77(26). Anal.calcd.for $C_{25}H_{19}NOCl_2$: C, 71.60; H, 4.53; N, 3.34; found C, 71.61; H, 4.56; N, 3.35.

4e solid, m.p

102-^{0}C. ^{1}H NMR(DMSO): δ3.17(dd, J=7.2, 17.6 Hz, 2H), 3.40(dd, J=7.2, 18.2Hz, 2H), 5.11(t, J=7.4 Hz, 2H), 6.88-7.40(m, 18H), 10.88(s, 2H, NH)ppm. m/z(%): 293(9), 253(20), 240(100), 204(81), 176 (37), 143(2), 130(10), 117(8), 102(12), 89(5), 75 (11). Anal.calcd. for $C_{33}H_{26}N_2OCl_2$: C, 73.88; H, 4.85; N, 3.34; found C, 73.89; H, 4.87; N, 3.36.

3f viscous liquid

^{1}H-NMR(DMSO): δ3.45(dd, J=7.6, 16.4 Hz, 1H), 3.62(dd, J=7.6, 16.4Hz, 1H), 4.86(t, J=7.6 Hz, 1H), 6.92-7.66(m, 15H), 10.93(s, 1H, NH) ppm.m/z (%): 421(66), 419(100), 356(11), 254(60), 240(94), 204 (20), 178(12), 137(25), 115(24), 102(44), 89(10), 77 (15). Anal. calcd. for $C_{25}H_{19}NOCl_2$: C, 71.60; H 4.53; N, 3.34; found C, 71.64; H, 4.56; N, 3.37.

4f viscous liquid

^{1}H-NMR(DMSO): δ3.24(dd, J=7.6, 15.2 Hz, 2H), 3.32(dd, J=7.6, 15.2Hz, 2H), 4.63(m, 2H), 6.89-7.39 (m, 18H), 10.88 (s, 2H, NH) ppm. m/z=537 (5),

254(25), 240(100), 217(21), 204(68), 144(10), 130(17), 117(21), 104(18), 89(20), 77(19). Anal. calcd. for $C_{33}H_{26}N_2OCl_2$: C 73.88, H 4.85, N 3.34; found C 73.90, H 4.87, N 3.36.

3g viscous liquid

^{1}H-NMR(Acetone-d_6): δ3.50(dd, J=8.0, 16.0 Hz, 1H), 3.63(dd, J=7.2, 16.0Hz, 1H), 4.99(t, J=8.0 Hz, 1H), 6.92-7.70(m, 15H), 10.11(s, 1H, NH) ppm. m/z (%): 421(65), 419(100), 356(5), 254(45), 240 (89), 204(25), 178(17), 165(24), 137(77), 115(54), 102 (99), 89(24), 77(38). Anal. calcd. for $C_{14}H_{12}O_2Br_2$: C 45.16, H 3.23; found C 45.19, H 3.24. Anal.calcd.for $C_{25}H_{19}NOCl_2$: C 71.60, H 4.53, N 3.34; found C 71.63, H 4.57, N 3.37.

4g viscous liquid

^{1}H-NMR(Acetone-d_6): δ3.24(dd, J=8.0, 16.8Hz, 2H), 3.36 (dd, J=7.6, 16.8Hz, 2H), 4.83(t, J=8.0 Hz, 2H), 7.06-7.39(m, 18H), 10.07(s, 2H, NH)ppm. m/z=536(3), 254(18), 240(100), 218(41), 204(80), 144(30), 130(15), 117(25), 89(21), 77(12), 55(57). Anal.calcd.for $C_{33}H_{26}N_2OCl_2$: C,73.88; H, 4.85; N, 3.34; found C, 73.91; H, 4.88; N 3.36.

3h viscous liquid

^{1}H NMR(DMSO): δ3.45 (dd, J=7.6, 16.4Hz, 1H), 3.61(dd, J=7.6, 16.2 Hz, 1H), 4.84(t, J=7.6 Hz, 1H), 6.92-7.70(m, 15H), 10.92(s, 1H, NH)ppm. ppm.m/z(%): 392(12), 204(3), 130(3), 115(4), 102 (100), 76(22). Anal.calcd.for $C_{14}H_{12}O_2Br_2$: C 45.16, H 3.23; found C 45.19, H 3.24. Anal.calcd.for $C_{25}H_{19}NOBr_2$: C, 58.94, H, 3.73, N, 2.75; found C 58.96, H, 3.75, N, 2.78.

4h viscous liquid

^{1}H-NMR(DMSO): δ3.23(dd, J=7.8, 15.2Hz, 2H), 3.31(dd, J=7.8, 15.2Hz, 2H), 4.63((t, J=8.0Hz, 2H), 6.89-7.61(m, 18H), 10.88(s, 2H, NH)ppm.m/z(%): 626(21), 509(3), 340(29), 299(32), 284(100), 204 (59), 178(12), 143(15), 130(55), 115(10), 102(11), 89(2), 77(3). Anal.calcd.for $C_{33}H_{26}N_2OBr_2$: C, 63.26; H, 4.15; N, 4.47; found C, 63.29; H, 4.17; N, 4.48.

3i solid, m.p

125-127 °C. ^{1}H-NMR (DMSO): δ3.43(dd, J=8.0, 16.8 Hz, 1H), 3.59(dd, J=7.2, 16.4 Hz, 1H), 4.82(t, J=7.6 Hz, 1H), 6.90-7.67(m, 15H), 10.91(s, 1H, NH) ppm. m/z (%): 392(12), 204(3), 130(3), 115(4), 102(100), 76(22). Anal.calcd.for $C_{14}H_{12}O_2Br_2$: C 45.16, H 3.23; found C 45.19, H 3.24. Anal. calcd. for $C_{25}H_{19}NOBr_2$: C, 58.94; H, 3.73; N, 2.75; found C, 58.97; H, 3.75; N, 2.78.

4i solid, m.p

162-164 °C. ^{1}H-NMR (Acetone-d_6): δ3.24(dd, J=8.0, 16.8 Hz, 2H), 3.37 (dd, J=8.0, 16.8 Hz, 2H), 4.81 (t, J=8.0Hz, 2H), 7.06-7.75(m, 18H), 10.08(s, 2H, NH) ppm.m/z (%): 626(28), 509(5), 392(12), 342 (20), 299(15), 284(41), 204(31), 178(11), 144 (15), 130(48), 117(28), 102(62), 89(23), 28(100). Anal. calcd. for $C_{33}H_{26}N_2OBr_2$: C, 63.26; H, 4.15; N, 4.47; found C, 63.30; H, 4.18; N, 4.48.

3j viscous liquid

^{1}H-NMR (Acetone-d_6): δ3.84(dd, J=8.0,16.4 Hz, 1H), 3.94(dd, J=8.0, 16.4Hz, 1H), 5.31(t, J=8.0 Hz, 1H), 7.18-8.36(m, 15H), 10.25(s, 1H, NH) ppm. m/z (%): 324(47), 277(19), 245(73), 232(26), 220(29), 206 (51), 176(83), 144(18), 130(68), 115(30), 102(75), 90(36), 76 (30). Anal. calcd. for $C_{25}H_{19}N_3O_5$: C, 71.26, H, 4.51, N, 9.98; found C, 71.28, H, 4.54, N, 9.99.

4j viscous liquid. ^{1}H NMR (Acetone-d_6)

δ3.68 (dd, J=8.0, 16.4 Hz, 2H), 3.78 (dd, J=7.2, 16.8 Hz, 2H), 5.15 (t, J=8.0Hz, 2H), 7.05-8.26(m, 18H), 10.22(s, 2H, NH); ppm. m/z (%): 245(100), 233(5), 217(8), 189(3), 130(3), 117(9), 77(5). Anal. calcd. for $C_{33}H_{26}N_4O_5$: C, 73.60; H, 4.83; N, 10.42; found C, 73.62; H, 4.86; N, 10.46.

RESULT AND DISCUSSION

The effect of the reaction conditions on the conjugate addition of indole with 1,5-diaryl-1,4-pentadien-3-ones under ultrasound irradiation is summarized in TABLE 1. We firstly monitored the effects of frequencies of ultrasound irradiation on the reaction and found that higher yields were obtained at lower frequencies. For example, when the frequency was 25 kHz the desired product was obtained in 72% yield within 30min(Entry b), while upon sonication with a

TABLE 2 : Michael addition of indole to 1,5-diaryl-1,4-pentadien-3-ones catalyzed by PTSA under ultrasound

Entry	Ar	Time, min	Isolated yield, %	
			Overall	3/4
a	C_6H_5	30	98	35/63
b	p-$(CH_3)_2NC_6H_4$	45	94	54/40
c	p-$CH_3OC_6H_4$	60	86	50/36
d	p-$CH_3C_6H_4$	60	98	46/52
e	o-ClC_6H_4	90	80	47/33
f	m-ClC_6H_4	90	93	48/45
g	p-ClC_6H_4	90	94	53/41
h	m-BrC_6H_4	90	90	53/37
i	p-BrC_6H_4	110	77	53/24
j	p-NO_2 C_6H_4	120	5	3/2

frequency of 59 kHz, the Michael addition reaction afforded the desired product in only 62% yield within 30min(Entry d). We also did the experiment in the absence of ultrasound, the reaction of indole with 2a gave only 55% yield at room temperature using stirring within 30 min in anhydrous ethanol(Entry a). It is clear that the ultrasound can accelerate the Michael addition of indole to 1,5-diaryl-1,4-pentadien-3-ones. As a result of these findings, our work was carried out under 25 kHz ultrasonic irradiation.

As shown in entries b, e and f of TABLE 1, increasing the quantity of the catalyst can improve the yields. For example, when the amount of the catalyst is 100mol%, total yield of 3 and 4 was 72% within 30 min, whereas increasing the amount of the catalyst to 200mol%, the yield was 82% within 30min. So the amount of the catalyst we chose was 200mol%.

We also studied the influence of the different molar ratio of 1:2:PTSA on the Michael addition (TABLE 1, Entries f-i). We found the reaction condition of indole(1.75mmol), 1,5-diaryl-1,4-pentadien-3-ones (1mmol), PTSA(2mmol) gave the best yield (98%, Entries h). On the base of these results, the molar ratio of 1:2:Cat. We chose was 1:1.75:2. The results of a series of the reactions of indole and 1,5-diaryl-1,4-pentadien-3-ones were summarized in TABLE 2.

In Ji's reported the conjugation of indole and chalcones catalyzed by PTSA gave excellent yields within 1.5-4 h[11]. We extended this reaction to indole conjugated addition with dichalcones. As shown in TABLE 2 indole and 1,5-diaryl-1,4-pentadien-3-ones via Michael addition can give good yields under ultrasound irradiation. For example, 1,5-diphenzyl-1,4-pentadien-3-one(2a) as the substrate, the yield was up to 98%(3a+4a) within 30 min under ultrasonic irradiation. Arcadi et al. described the Michael addition of indole with 1,5-diphenzyl-1,4-pentadien-3-ones(2a) catalyzed by $NaAuCl_4 2H_2O$ to afford the mono-additive product 3a in 65% yield within 1.5 h[15]. In our procedure, the corresponding product was obtained in 98% yield(3a+4a) within 30 min under ultrasonic irradiation.

The substituents in the benzene ring have some effects on the yields. The electron-donating substituents in the benzene ring(TABLE 2, b-d) can increase the reactivity of Michael addition. In contrast, electron-withdrawing substituents decreased the reactivity(TABLE 2, e-j). It is indicated that electron-with drawing substituents can decrease the electronic cloud density on 1,4-position in 1,5-diaryl-1, 4-pentadien-3-ones, then increase the electrophilicity in the conjugate addition. In addition, we found that substituents in the benzene ring inhibited the reactivity and decreased the conversion of the reaction because of the steric hinderance(TABLE 2).

The reaction of indole with 1,5-diaryl-1,4-pentadien-3-ones could afford two of the mono-additive and bis-additive products. As can be seen from Table 2, 2b, 2c, and 2e-2j as substrates, the corresponding yields of the bis-additive products 4b, 4c and 4e-4j were higher than those of the mono-additive products. In the reaction of indole 1a with 2a and 2d, the yields of mono-additive products were higher under the same conditions. In present system, the chemical selectivity was moderate, the reason was not clear.

In conclusion, the ultrasound can accelerate the Michael addition of indole to 1,5-diaryl-1,4-pentadien-3-ones, the overall yield can reach 98% (TABLE 2a), but the chemical selectivity was unsatisfactory.

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