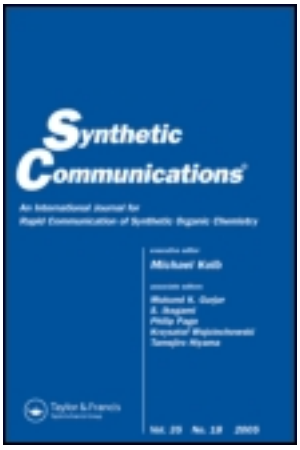

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A Microwave Promoted New Condensation Reaction of Aryl Ketones With Triethyl Ortho-Formate

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A MICROWAVE PROMOTED NEW CONDENSATION REACTION OF ARYL KETONES WITH TRIETHYL ORTHO-FORMATE

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Abstract: Under microwave irradiation, boron trifluoride has been found to mediate a new condensation reaction of aryl ketones with triethyl orthoformate to give a series of new products (C1-C10) is described. The compounds were first reported. Their structure were determined by IR, MS, and ^{1}H /^{13}C NMR spectra.

There is considerable current interest in organic reactions under microwave irradiation [1]. Some reactions which need long reaction time to reach completion (e.g. several hours or several days) could be carried out in several minutes under microwave promotion [2-5], and in some cases new reactions were found [6]. Generally, acetals are usually obtained when triethyl orthoformate reacts

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with various ketones under acidic conditions [7,8], but in the same situation an abnormal reaction took place under microwave irradiation (750W × 70% 2450Hz), and a series of new compounds (C1-C10) were obtained from arylketones (S1-S10) mixed with triethyl orthoformate mediated by boron trifluoride etherate.

All the compounds obtained gave elemental analyse for C and H in good agreement to calculated values. The structures of the products were confirmed by IR, MS, and ^{1}H /^{13}C NMR spectra.

The reaction implies that microwave radiation plays an important role to change the reaction pathway in the process of condensation, and steric hindrance of the substrates influence the structure of the products, although the mechanism of the reaction is not yet clear. When existed a small group in the substrates, such as S1-S9, obtained triaroyl methane (C1-C9). When existed a bulky group in substrate, such as S10, obtained a fused cyclopentenone ring compound, i.e. 7-methoxy-1-[1-(6-methoxynaphthoyl)-ethyl]-2-methyl-2,3-dihydro-1H-cyclopenta [α] naphthalen-3-one.

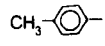
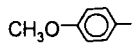
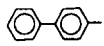
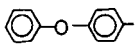
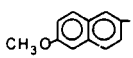
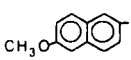
Experimental

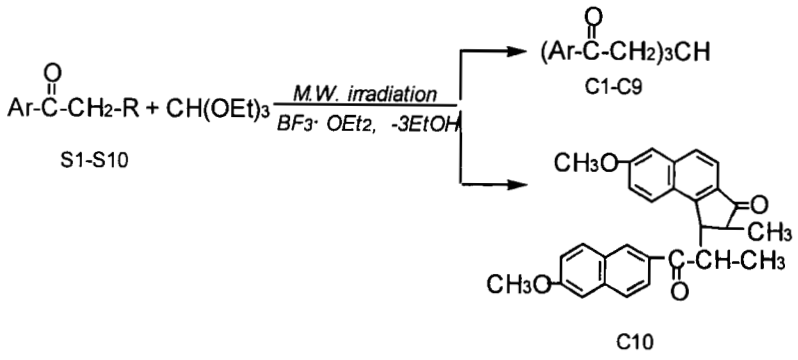
Microwave irradiation was carried out with a commercial microwave oven National nw-525.5, and it was refit according as literature[9]. Melting points were determined on an XT_4 microscope melting point apparatus and uncorrected. IR spectra were recorded in KBr on a Nicolet-10DX FT-IR spectrophotometer (ν max in cm^{-1}). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were measured on a Varian-FT-400 instrument using $CDCl_3$ as solvent and TMS as internal reference (chemical shifts in ppm). MS spectra were recorded on a ZAB-HS spectrometer. Microanalyses were obtained with Carlo-Erba 1160 instrument.

General procedure:

Boron trifluoride etherate liquid (0.05 mol) was added to a mixture of the arylketone (0.5 mol) and triethyl orthoformate (1.0 mol). The solution was put into the microwave reactor. After

Table 1. Preparation of Compounds(C)

Entry.	Ar-	R	T (time)	Yield (%)	Mp (°C)	Molecular. formula	element analysis C	(Calc.) H
1		H	8	83	140-141	$C_{25}H_{22}O_3$	81.05(81.06),	5.99(5.97)
2		H	8	85	183-184	$C_{28}H_{28}O_3$	81.54(81.52),	6.87(6.84)
3		H	8	81	172-173	$C_{28}H_{28}O_6$	73.08(73.02),	6.17(6.13)
4		H	10	75	158-159	$C_{25}H_{19}O_3Cl_3$	63.41(63.38),	4.10(4.06)
5		H	10	79	163-164	$C_{25}H_{19}O_3Br_3$	49.43(49.46),	3.12(3.15)
6		H	8	59	195-196	$C_{43}H_{34}O_3$	86.30(86.26),	5.77(5.72)
7		H	8	55	179-180	$C_{43}H_{34}O_6$	79.89(79.86),	5.28(5.30)
8		H	8	58	168-169	$C_{40}H_{34}O_6$	79.71(78.67),	5.64(5.61)
9		CH_3	8	71	138-139	$C_{31}H_{34}O_3$	81.96(81.90),	7.49(7.54)
C10		CH_3	8	79	187-188	$C_{29}H_{26}O_4$	79.42(79.43),	5.96(5.98)



Scheme 1

irradiating and refluxing, the reaction mixture was cooled to room temperature, poured into vigorously stirred water (500 ml), and then extracted with dichloromethane (5×200 ml). The organic phase was washed with water (3×100 ml), dried ($MgSO_4$), filtered and concentrated. The solid residue was purified via silica gel column chromatography with petroleum ether (60-90℃)-dichloromethane(4:1) as eluent. The pure compound was obtained. The spectral data of C1-C10 are as follow:

C1. IR: 1676; ^{1}H NMR: 3.26(d, 6H), 3.35(m, 1H), 7.44(m, 6H), 7.54(m, 3H), 8.00(m, 6H); ^{13}C NMR: 27.60, 42.35(3C), 128.17(6C), 128.59(6C), 133.17(3C), 136.76(3C), 199.44(3C). MS (FAB): 371(M^++1); (EI, 70ev): 352, 251, 250, 233(100), 173, 145, 121, 120, 106, 105, 77.

C2. IR: 1674; ^{1}H NMR: 2.39(s, 9H), 3.20(d, 6H), 3.31(m, 1H), 7.23(d, 6H), 7.90(d, 6H); ^{13}C NMR: 20.75(3C), 27.59, 43.18(3C), 128.22(6C), 129.07(6C), 137.66(3C), 139.58(3C), 199.61(3C); MS (FAB): 413(M^++1); (EI, 70ev): 394, 279, 278, 261, 187, 159, 134, 119(100), 116, 91, 77, 65.

C3. IR: 1674; ^{1}H NMR: 3.18(d, 6H), 3.30(m, 1H), 3.84(s, 9H), 7.27(d, 6H), 7.94(d, 6H); ^{13}C NMR: 28.61, 43.56(3C), 55.72(3C), 114.93(6C), 128.42(6C), 136.22(3C), 159.28(3C), 200.02(3C); MS (FAB): 461(M^++1); (EI, 70ev): 442, 311, 293, 150, 135(100), 107, 93, 77, 65.

C4. IR: 1674; ^{1}H NMR: 3.21(d, 6H), 3.25(m, 1H), 7.44(d, 6H), 7.85(d, 6H); ^{13}C NMR: 27.52,

42.55(3C), 129.62(6C), 130.78(6C), 132.16(3C), 137.47(3C), 199.56(3C); MS (FAB): 473(M^++1), 475(M^++2+1); (EI, 70ev): 456, 454, 321, 319, 303, 301, 181, 179, 156, 154, 141, 139(100), 113, 111, 77, 75.

C5. IR: 1674; ^{1}H NMR: 3.21(d, 6H), 3.35(m, 1H), 7.60(d, 6H), 7.87(d, 6H); ^{13}C NMR: 27.54, 42.93(3C), 128.32(6C), 130.01(6C), 131.84(3C), 136.12(3C), 199.59(3C); MS (FAB): 605, (M^++1), 607(M^++2+1); (EI, 70ev): 588, 586, 409, 408, 407, 406, 391, 389, 253, 251, 200, 198, 185(100), 183, 157, 155, 77, 75.

C6. IR: 1676; ^{1}H NMR: 3.21(d, 6H), 3.31(m, 1H), 7.00-8.02(m, 27H); ^{13}C NMR: 27.68, 42.31(3C), 126.02(6C), 126.17(6C), 126.28(6C), 127.46(3C), 128.99(6C), 139.40(3C), 139.79(3C), 143.01(3C), 202.58(3C); MS (FAB): 599, (M^++1); (EI, 70ev): 580, 579, 385, 250, 222, 196, 181, 153, 152, 77 (100).

C7. IR: 1676; ^{1}H NMR: 3.19(d, 6H), 3.29(m, 1H), 6.93-7.92(d, 27H); ^{13}C NMR: 27.64, 42.42(3C), 117.59(3C), 117.76(3C), 118.91(6C), 123.63(3C), 127.31(3C), 127.42(3C), 130.09(6C), 138.77(3C), 156.23(3C), 156.44(3C), 203.16(3C); MS (FAB): 647(M^++1); (EI, 70ev): 628, 435, 417, 266, 238, 212, 197, 169, 120, 105, 93, 77(100), 65.

C8. IR: 1678; ^{1}H NMR: 3.21(m, 1H), 3.37(d, 6H), 3.97(s, 9H), 7.12-8.44(m, 24H); ^{13}C NMR: 27.61, 43.28(3C), 55.28(3C), 105.58(3C), 119.03(3C), 121.25(3C), 124.35(3C), 126.62(3C), 127.53(3C), 129.01(3C), 133.14(3C), 138.82(3C), 159.49(3C), 201.63(3C); MS (FAB): 611, (M^++1); (EI, 70ev): 592, 411, 393, 254, 226, 200, 185(100), 157, 142, 126.

C9. IR: 1679; ^{1}H NMR: 1.35(d, 9H), 2.36(s, 9H), 3.18(m, 3H), 3.32(m, 1H), 7.27(d, 6H), 7.96(d, 6H); ^{13}C NMR: 15.42(3C), 20.69(3C), 29.63, 44.17(3C), 128.28(6C), 128.84(6C), 137.72(3C), 140.13(3C), 202.46(3C); MS (FAB): 455, (M^++1); (EI, 70ev): 436, 306, 305, 288, 215, 148, 119(100), 91, 77, 65.

C10. IR: 1705, 1665; ^{1}H NMR: 1.34(d, 3H), 1.47(d, 3H), 3.02(m, 1H), 3.85(m, 1H), 3.89(s, 3H), 3.91(s, 3H), 4.31(m, 3H), 6.89-8.18(m, 11H); ^{13}C NMR: 17.53, 19.16, 44.60, 46.35, 50.17, 55.31,

55.41, 105.39, 107.45, 119.10, 119.35, 120.30, 124.31, 125.64, 126.35, 126.67, 127.12, 128.00, 129.14, 130.63, 131.69, 132.15, 136.79, 138.79, 155.20, 159.52, 159.61, 202.40, 208.10; MS (EI, 70ev): 438(M^+), 253, 225, 214(100), 197, 185, 157, 142, 126, 125, 114.

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