J. Iran. Chem. Soc., Vol. 6, No. 4, December 2009, pp. 761-768.

JOURNAL OF THE
Iranian
Chemical Society

Poly(*N*,*N*′-dichloro-*N*-ethyl-benzene-1,3-disulfonamide, *N*,*N*,*N*′,*N*′-tetrachlorobenzene-1,3-disulfonamide, Poly(*N*,*N*′-dibromo-*N*-ethyl-benzene-1,3-disulfonamide, and *N*,*N*,*N*′,*N*′-Tetrabromobenzene-1,3-disulfonamide Catalyzed Formylation of Amines and Alcohols Using Ethyl Formate under Microwave Irradiation

R. Ghorbani-Vaghei*, H. Veisi and M. Amiri
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

(Received 15 February 2008, Accepted 24 October 2008)

A simple, rapid, and efficient procedure for formylation of primary and secondary amines and alcohols using ethyl formate catalyzed with poly(*N*,*N*′-dichloro-*N*-ethyl-benzene-1,3-disulfonamide (PCBS), *N*,*N*,*N*′,*N*′-tetrachlorobenzene-1,3-disulfonamide (TCBDA), poly(*N*,*N*′-dibromo-*N*-ethyl-benzene-1,3-disulfonamide (PBBS) and also *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide (TBBDA) was adopted. The reactions were performed under microwave irradiation with high yields.

Keywords: Formylation, Amines and alcohols, Microwave irradiation, 1,3-Disulfonamide and poly(1,3-disulfonamide) derivatives

INTRODUCTION

Formylation of alcohols and amines is an important transformation in organic synthesis and provides an efficient method for protection of OH and NH groups. *N*-Formyl compounds have been widely used in organic synthesis as protecting group of amines [1], an intermediate for mono methylated amines from primary amines [2], catalyst for allylation, or reduction [3]. They have been also widely used in the synthesis of pharmaceutically important compounds such as fluroqninolones [4], substituted aryl imidazoles [5], 1,2-dihydroqninolines [6] and nitrogen bridged heterocycles [7], *etc*. Thus, various formylating methods have been reported for the preparation of formylated compounds. Acetic formic anhydride [1,8,9] is one of the most widely used formylating agents. However, because of its sensitivity to atmospheric moisture, it decomposes to acetic acid and carbon monoxide. Other useful formylating agents include chloral [10], activated formic acid using DCC [11] or EDCI [12], activated formic esters [13-16], ammonium formate [17] and formic acid itself (under reflux) [18-20].

A variety of catalysts have been used for activating this reagents, such as $Sc(OTf)_3$ and $Sc(NTf_2)_3$ [21], $TiCl(OTf)_3$ [22], TMSCl and TMSOTf [23], La(i-Pr)$_3$ [24], $COCl_2$ [25], $Sn(OTf)_2$ [26], $TiCl_4$ and $AgClO_4$ [27], $AlPW_{12}O_{40}$ [28], PCl_3-$n(SiO_2)_n$ [29], PPh_3/CBr_4 [30] $K_5CoW_{12}O_{40}.3H_2O$ [31], CCl_3CHO/K_2CO_3 [32] and ZnO [33].

Some of the reagents reported for formylation are often hazardous, very toxic, expensive, not readily available, need to be freshly prepared, and in some cases, the reaction requires drastic conditions or prolonged reaction times and tedious work-up. Thus, milder, non-hazardous, and inexpensive reagents are still in demand.

*Corresponding author. E-mail: rgvaghei@yahoo.com

EXPERIMENTAL

Procedure for the Preparation of Poly(*N*,*N*'-dichloro-*N*-ethyl-benzene-1,3-disulfonamide) and *N*,*N*,*N*',*N*'-Tetrachlorobenzene-1,3-disulfonamide

A sample of white finely powdered poly(*N*-ethyl-benzene-1,3-disulfonamide) (1 g) or benzene-1,3-disulfonamide (1 g) was dissolved in the solution of NaOCl (14%), at room temperature for 30 min. The color of the solution did not change. Then, acetic acid (20 ml, 50%) was added to the solution. The insoluble chlorinated reagent was removed by filtration and washed with water (5 ml).

Analytical data for *N*,*N*,*N*',*N*'-tetrachlorobenzene-1,3-disulfonamide: white solid, m.p.: 145 °C, IR (KBr): 3050, 2950, 2900, 1570, 1462, 1417, 1377, 1304, 1167, 1082, 807, 776, 675 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 7.95-8.09 (m, CH aromatic, 1H), 8.11-8.58 (m, CH aromatic, 2H), 8.79 (s, CH aromatic, 1H), m/e ($[M+H]^+$): 375, 339, 337, 321, 319, 305, 303, 272, 269, 267, 156, 154, 139, 125, 120, 104, 91, 77, 63. Anal. Calcd. for $C_6H_4N_2S_2O_4Cl_4$: C, 19.25; H, 1.06; N, 7.48; S, 17.11, Cl, 37.96. Found: C, 19.32; H, 0.95; N, 6.95; S, 17.00, Cl, 37.16.

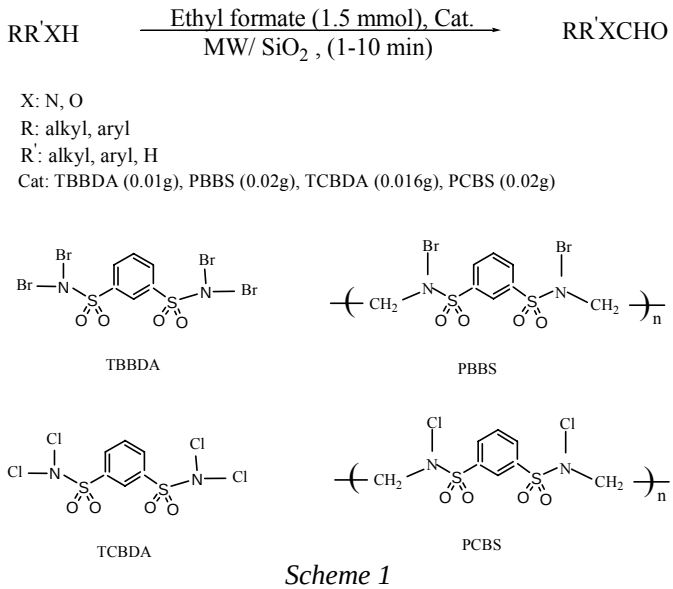
Analytical data for poly(*N*,*N*'-dichloro-*N*-ethyl-benzene-1,3-disulfonamide): white solid, m.p.: 175 °C, IR (KBr): 3050, 2950, 2900, 1578, 1462, 1418, 1377, 1303, 1168, 1081, 809, 779, 674, 603, 570 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 7.56-8.48 (b, CH aromatic).

Formylation of Amines and Alcohols

Amine or alcohol (1 mmol), ethyl format (1.5 mmol), catalyst [PBBS (0.02 g), TBBDA (0.02 mmol, 0.01 g), PCBS (0.02 g) or TCBDA (0.02 mmol, 0.016 g)] and SiO_2 (0.5 g) were added to a round-bottomed flask (25 ml). The flask was placed in a bath containing SiO_2 to enable absorption of additional microwave irradiation. The flask was irradiated in a microwave oven at a power output of 900 W (LG Co. microwave, 230 v ~ 50 Hz, RF output 900 W) at 110 °C. After completion of the reaction, [1-10 min, Table 1, monitored by TLC (3:1, *n*-hexane/acetone)], CH_2Cl_2 (10 ml) was added, and the catalyst was removed by filtration. Evaporation of the solvent under reduced pressure gave the product. Further purification was achieved by crystallization with ethanol.

RESULTS AND DISCUSSION

We now report a rapid and convenient method for formylation of amines and alcohols using ethyl format under microwave irradiation. The reactions were performed in high yields and catalyzed with novel reagents PCBS, TCBDA and PBBS, TBBDA [34-40] (Scheme 1).



Scheme 1

Initially, we carried out the reaction of benzyl amine with ethyl format under various conditions (i. in solvent at r.t., ii. thermal and iii. microwave) in the presence of novel reagent (TCBDA). We found that the best result (98% yield) could be obtained under microwave conditions.

Since PBBS, TBBDA, PCBS and TCBDA contain halogen atoms which are attached to the nitrogen atom, it is quite possible that they release Br^+ or Cl^+ *in situ* and act as Lewis acid to activate ethyl format in the reaction medium. We hoped that this would be sufficient to catalyze the formylation of amines and alcohols by ethyl format under microwave condition.

To explore the generality and scope of this reaction, a wide range of structurally varied alcohols, amines and thiols were subjected to formylation catalyzed by these halogenated compounds. The results are reported in Table 1. In this manner, we succeeded to develop convenient and efficient procedure for the preparation of formamides (Table 1, entries 1-21). Table 1 shows that the yields are high. Aromatic and aliphatic primary and secondary amines can react under this condition. For a variety of amines, *e.g.*, hindered amines (Table 1, entries 9, 10, 11, 14), heterocyclic amines (Table 1, entries 12, 15),

Poly(*N*,*N*′-dichloro-*N*-ethyl-benzene-1,3-disulfonamide

Table 1. Formylation of Alcohols and Amines with Ethyl Format under Microwave Irradiation Using PBBS, TBBDA, PCBS and TCBDA as Catalyst

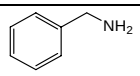
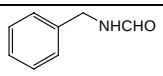
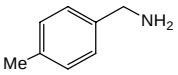
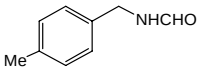
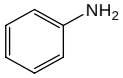
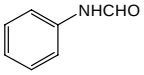
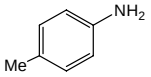
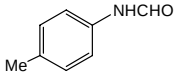
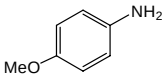
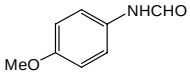
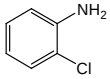
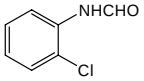
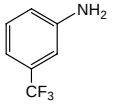
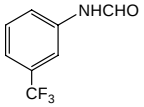
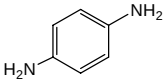
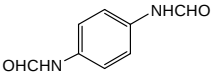
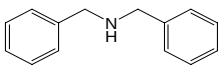
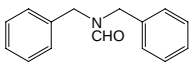
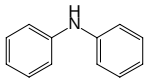
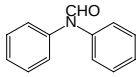
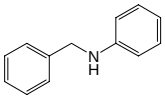
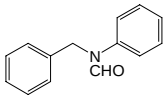
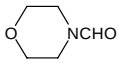
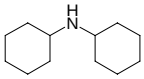
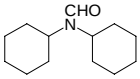
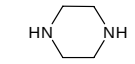
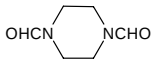
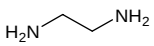
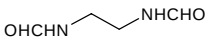
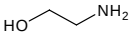
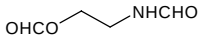
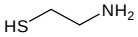
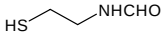
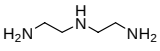
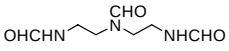
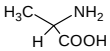
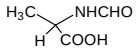
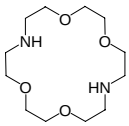
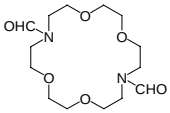
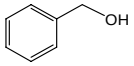
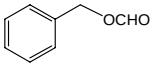
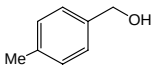
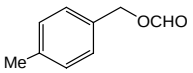
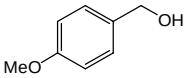
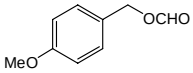
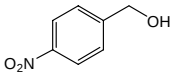
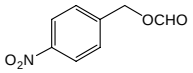
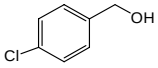
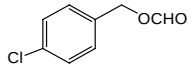
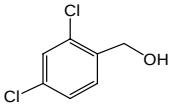
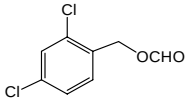
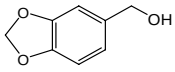
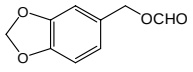
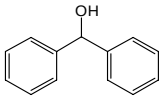
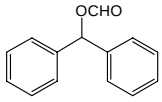
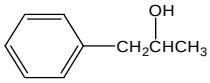
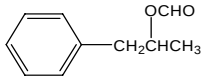
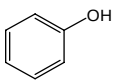
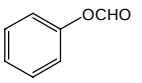
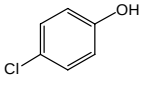
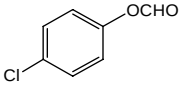
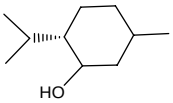
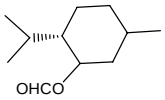
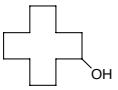
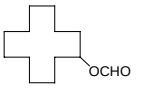
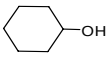
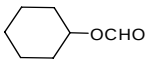
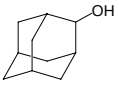
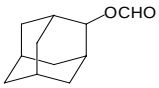
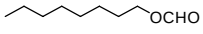
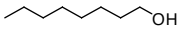
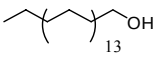
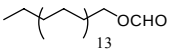
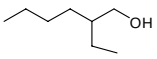
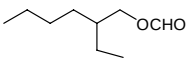
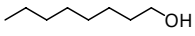
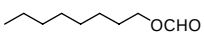
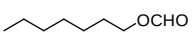
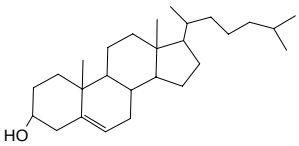
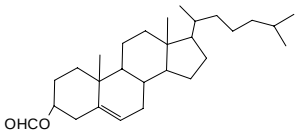
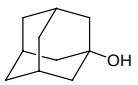
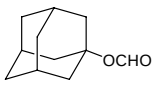
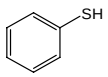
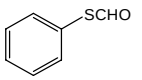
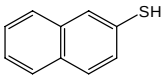
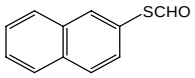
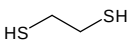
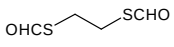
Entry	Substrate	Product	PBBS Time (min)/ yield (%)	TBBDA Time (min)/ yield (%)	PCBS Time (min)/ yield (%)	TCBDA Time (min)/ yield (%)	References for known compounds
1			1/98	1/99	1/98	1/98	[29]
2			1/98	1/100	1/96	1/96	[29]
3			4/98	3.5/99	4/96	5/95	[29]
4			4/96	3/98	4/95	5/95	[17]
5			3.5/96	3/99	4/96	4/95	[29]
6			4.5/96	3/98	4.5/96	4/96	[33]
7			3.5/96	3/99	3/96	3.5/95	-
8			4.5/90	3/92	4.5/90	4/90	-
9			1/98	1/99	1/96	1/96	[20]
10			2.5/96	2/98	2.5/96	2.5/95	[20]
11			1/96	0.5/98	1/96	1/96	[20]
12			1/98	1/100	2/98	1/98	[20]
13			1/96	0.5/98	1/96	1/96	[20]
14			1.5/92	1/96	1/92	1/92	[20]

Table 1. Continued

15			1/98	0.5/99	1/98	1/98	[20]
16			1/96	1/98	1/92	1/92	-
17			2/96	2/99	2/96	2/92	-
18			1/98	0.5/99	1/96	1/92	-
19			3/95	3.5/96	3/96	3.5/92	-
20			5/96	4/98	4/92	4/90	-
21			4/96	3/98	4/90	4/80	-
22			1/98	0.5/99	1/98	1/96	[29]
23			2/98	1/99	2/96	2/96	-
24			1/98	0.5/99	1/92	1/92	[29]
25			2/98	1/99	1/96	1/95	-
26			1/96	1/99	1/95	1/96	[29]
27			2/95	0.5/98	1/90	1/90	-
28			2/92	1/98	1/90	1/90	-
29			3/96	2/99	2/92	2/90	-
30			3/95	3.5/96	3/92	3.5/92	-

Poly(*N*,*N'*-dichloro-*N*-ethyl-benzene-1,3-disulfonamide

Table 1. Continued

31			10/55	10/60	10/50	10/50	-
32			10/50	10/45	10/45	10/45	-
33			3/95	3/96	3/92	3.5/92	[29]
34			3/90	3.5/96	3/80	3.5/80	-
35			3/92	3.5/96	3/85	4/85	[29]
36			5/90	4/96	5/87	5/85	-
37			4/90	3/92	3/80	3.5/80	-
38			3/95	3.5/96	3/92	3.5/92	-
39			4/95	4/96	3/90	3.5/90	-
40			4/90	4/90	3/90	3.5/90	-
41			10/96	10/98	10/90	10/90	-
42			3/96	2/99	2/96	2/96	[29]
43			10/0	10/0	10/0	10/0	-
44			10/0	10/0	10/0	10/0	-
45			10/0	10/0	10/0	10/0	-
46			10/0	10/0	10/0	10/0	-

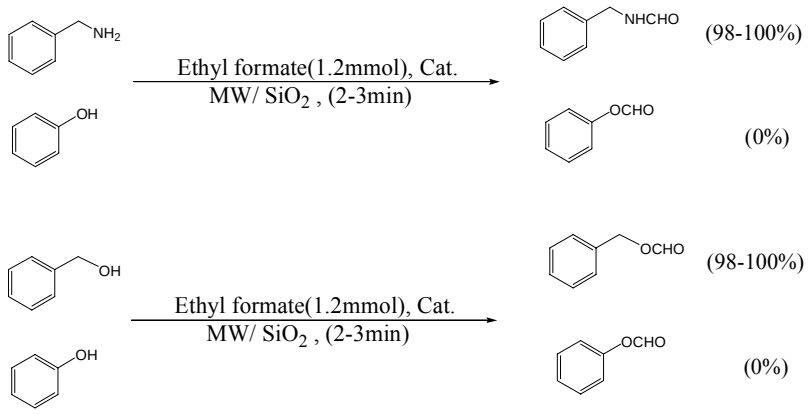
Products were characterized by comparison of their physical properties and spectral data with those of authentic samples.

amino acid (Table 1, entries 20), macrocyclic (Table 1, entry 21), diamines (Table 1, entries 15, 16), and triamine (Table 1, entries 19), the reaction shows good results without any significant influence of their structures on the product yields. Reactions of aromatic amines bearing both electron-donating and withdrawing groups proceed smoothly to give the corresponding *N*-formyl compounds in quantitative yields (Table 1, entries 1-8). Primary amines are easily formylated to provide their corresponding formamide in shorter reaction time and higher yields than secondary amines. There was no selectivity between primary and secondary amino groups during the reaction (Table 1, entry 19).

In a similar manner, various substituted aromatic and aliphatic hydroxyl groups were formylated very smoothly under mild reaction conditions to give the desired O-formylated alcohols in high yields. These procedures are uniformly effective for formylation of primary saturated alcohols (Table 1, entries 37-41), benzylic alcohols (Table 1, entries 22-28) and secondary alcohols (Table 1, entries 29, 30, 33-36), phenols (Table 1, entries 31, 32). Colesterol, as an example of secondary cyclic alcohol, was also formylated in excellent yield (Table 1, entry 42). In this reaction, we did not observe chemoselectivity for the reaction of ethanol amine having bi-functional groups of NH and OH (Table 1, entry 17).

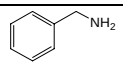
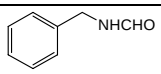
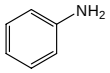
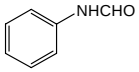
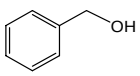
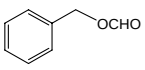
For comparison of the novel *N*-halo reagents with NBS for formylation under microwave irradiation, we performed this reaction with benzyl amine, aniline and benzyl alcohol. The results which are tabulated in Table 2 show that *N*-halo reagents function better than NBS for formylation of amines and alcohols under these conditions.

Our experiments also indicated that tertiary alcohols (Table 1, entry 43) and thiols (Table 1, entries 44-46) did not formylate under this condition, and this method is selective for the formylation of amines and alcohols in the presence of phenols (Scheme 2). Moreover, the results of Table 1 show that TBBDA catalyzes the reactions more efficiently than



Scheme 2

Table 2. Comparison of *N*-Halo Reagents with NBS in Formylation under Microwave Irradiation

Entry	Substrate	Product	TBBDA Time (min)/ yield (%)	TCBDA Time (min)/ yield (%)	NBS Time (min)/ yield (%)
1			1/99	1/98	2/90
3			3.5/99	5/95	8/92
22			1/98	1/96	3/95

other halogenated compounds.

Analytical Data for Selected Compounds

Compound (19). IR (KBr): 3280, 1675, 1462, 1410, 1277, 1140, 1019 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 3.13 (t, CH_2, 4H), 3.58 (t, CH_2, 4H), 5.84 (b, NH, 2H), 8.10 (s, CHO, 1H), 8.16 (s, CHO, 2H), m/e: 187, 186, 170, 169, 152, 129, 86, 70, 58, 56, 43, 39.

Compound (20). IR (KBr): 3378, 2950, 2727, 1921, 1724, 1377, 1605, 1517, 1460, 1300, 1231, 1207, 1121, 1065 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 1.27-1.35 (d, CH_3, 2H), 4.38 (q, CH, 1H), 6.68 (b, NH, 1H), 8.00 (s, CHO, 1H), m/e: 118, 90, 72, 44, 43, 42.

Compound (21). IR (KBr): 1668, 1463, 1378, 1320, 1211, 1121, 1001 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 3.46 (s, CH_2, 24H), 7.92 (s, CHO, 2H), m/e: 319, 291, 263, 215, 187, 160, 132, 100, 71, 56, 48.

Compound (18). IR (KBr): 3365, 2958, 2924, 2855, 2020, 1662, 1601, 1462, 1378, 1250, 1151, 1100, 1042, 978, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 2.35 (s, SH, 1H), 3.35 (s, CH_2, 2H), 3.65 (s, CH_2, 2H), 6.12 (b, NH, 1H), 8.06 (s, CHO, 1H)

Compound (7). IR (KBr): 3210, 2950, 1685, 1600, 1458, 1370, 1250, 1140, 1120, 1040, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 6.5-7.8 (m, CH aromatic, 4H), 7.8 (b, NH, 1H), 8.56 (s, CHO, 1H).

Compound (8). IR (KBr): 3293, 2980, 1690, 1603, 1450, 1377, 1250, 1159, 1011, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 6.8-7.8 (dd, CH aromatic, 4H), 7.9 (b, NH, 2H), 8.50 (s, CHO, 2H).

Compound (16). IR (KBr): 3270, 2956, 2854, 1668, 1462, 1160, 1020 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 3.46 (t, CH_2, 4H), 6.20 (b, NH, 2H), 8.12 (s, CHO, 2H).

Compound (17). IR (KBr): 3320, 3290, 2956, 2854, 1722, 1663, 1460, 1170, 1012 cm^{-1}, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 3.59 (t, CH_2, 2H), 4.27 (t, CH_2, 2H), 6.14 (b, NH, 1H), 8.05 (s, CHO, 1H), 8.8.12 (s, CHO, 1H).

Compound (23). IR (KBr): 3001, 2933, 1727, 1622, 1505, 1464, 1367, 1268, 1160, 1112, 1033, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 2.07 (s, CH_3, 3H), 4.27 (s, CH_2, 2H), 6.8-7.52 (dd, CH aromatic, 4H), 8.06 (s, CHO, 1H).

Compound (25). IR (KBr): 3033, 2933, 1734, 1690, 1522, 1463, 1377, 1250, 1154, 1114, 1014, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 5.26 (s, CH_2, 2H), 7.45-8.23 (dd, CH aromatic, 4H), 8.45 (s, CHO, 1H).

Compound (27). IR (KBr): 3094, 2927, 2855, 1730, 1592, 1564, 1475, 1365, 1242, 1161, 1104, 1004, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 5.22 (s, CH_2, 2H), 7.28-8.35 (m, CH aromatic, 3H), 8.11 (s, CHO, 1H).

Compound (28). IR (KBr): 3025, 2953, 1725, 1680, 1542, 1453, 1367, 1242, 1134, 1102, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 4.85 (s, CH_2, 2H), 5.85 (s, CH_2, 2H), 7.15-8.12 (m, CH aromatic, 3H), 8.22 (s, CHO, 1H).

Compound (29). IR (KBr): 3064, 3032, 2885, 1727, 1601, 1557, 1494, 1463, 1163, 1080, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 7.32 (s, CH aromatic, 10H), 8.23 (s, CHO, 1H).

Compound (30). IR (KBr): 3044, 2933, 1727, 1601, 1585, 1494, 1453, 1163, 1030, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 1.30 (d, CH_3, 3H), 2.87 (d, CH_2, 2H), 5.21 (m, CH, 1H), 7.24 (s, CH aromatic, 5H), 7.95 (s, CHO, 1H).

Compound (31). IR (KBr): 3074, 3025, 2875, 1725, 1610, 1545, 1494, 1445, 1162, 1041, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 7.52 (s, CH aromatic, 5H), 8.24 (s, CHO, 1H).

Compound (32). IR (KBr): 3070, 3023, 2845, 1724, 1600, 1565, 1487, 1456, 1153, 1054, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 7.52 (dd, CH aromatic, 4H), 8.30 (s, CHO, 1H).

Compound (34). IR (KBr): 2930, 2842, 1725, 1471, 1447, 1494, 1376, 1181, 1153, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 1.25 (s, CH_2, 22H), 5.06 (m, CH, 1H), 7.92 (s, CHO, 1H).

Compound (36). IR (KBr): 2952, 2876, 1731, 1466, 1340, 1178, 925, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 1.65-1.94 (m, CH aliphatic, 14H), 5.01 (s, CH, 1H), 8.07 (s, CHO, 1H).

Compound (37). IR (KBr): 2952, 2855, 1720, 1466, 1370, 1178, 917, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 0.82 (t, CH_3, 3H), 1.22 (m, CH_2, 12H), 4.09 (t, CH_2, 2H), 7.98 (s, CHO, 1H).

Compound (38). IR (KBr): 2952, 2876, 1711, 1466, 1360, 1176, 925, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 0.81 (t, CH_3, 3H), 1.20 (m, CH_2, 28H), 4.02 (t, CH_2, 2H), 7.94 (s, CHO, 1H).

Compound (39). IR (KBr): 2963, 2856, 1715, 1456, 1355, 1170, 915, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 0.85 (t, CH_3, 6H), 1.22 (m, CH aliphatic, 11H), 4.12 (d, CH_2, 2H), 7.90 (s, CHO, 1H).

Compound (40). IR (KBr): 2950, 2842, 1712, 1456, 1363, 1171, 925, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 0.90 (t, CH_3, 3H), 1.31 (m, CH_2, 10H), 4.10 (t, CH_2, 2H), 7.81 (s, CHO, 1H).

Compound (41). IR (KBr): 2956, 2852, 1716, 1466, 1371, 1168, 912, ^1H NMR ($CDCl_3$, FT-250 MHz): δ 0.85 (t, CH_3, 3H), 1.23 (m, CH_2, 8H), 4.02 (t, CH_2, 2H), 7.76 (s, CHO, 1H).

CONCLUSIONS

The microwave assisted formylation by ethyl format and our *N*-halo reagents as catalyst, provide an efficient, fast, convenient and easy work up procedure for the synthesis of mono- and disubstituted formyl groups.

ACKNOWLEDGEMENTS

We are thankful to Bu-Ali Sina University and Center of Excellence of Chemical Methods (CEDCM) for financial support.

REFERENCES

[1] J.C. Sheehan, D.D.H. Yang, J. Am. Chem. Soc. 80 (1958) 1154.
[2] L.G. Humber, J. Med. Chem. 14 (1971) 982.
[3] S. Kobayashi, K. Nishio, J. Org. Chem. 59 (1994) 6620.
[4] A. Jakson, O. Meth-Cohn, J. Chem. Soc., Chem. Commun. (1995) 1319.
[5] B.C. Chen, M.S. Bednarz, R. Zhao, J.E. Sundeen, P. Chen, Z. Shen, A.P. Skoumbourdis, J.C. Barrish, Tetrahedron Lett. 41 (2000) 5453.
[6] K. Kobayashi, S. Nagato, M. Kawakita, O. Morikawa, H. Konishi, Chem. Lett. (1995) 575.
[7] A. Kakehi, S. Ito, S. Hayashi, T. Fujii, Bull. Chem. Soc. Jpn. 68 (1995) 3573.
[8] T.W. Green, P.G.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed., Wiley-Interscience, New York, 1999.
[9] P. Strazzolini, A.G. Giumanini, S. Cauci, Tetrahedron 46 (1990) 1081.
[10] F.F. Blicke, C.J. Lu, J. Am. Chem. Soc. 74 (1952) 3933.
[11] J. Waki, J. Meienhofer, J. Org. Chem. 42 (1977) 2019.
[12] F.M.F. Chen, N.L. Benoiton, Synthesis (1979) 709.
[13] H.L.Yale, J. Org. Chem. 36 (1971) 3238.
[14] L. Kisfaludy, O. Laszlo, Synthesis (1987) 510.
[15] M. Neveux, C. Bruneau, P.H. Dixneuf, J. Chem. Soc. Perkin Trans. I (1991) 1197.
[16] W. Duczek, J. deutsch, S. Vieth, H.J. Niclas, Synthesis (1996) 37.
[17] P.G. Reddy, G.D.K. Kumar, S.Baskaran, Tetrahedron Lett. 41 (2000) 9149.
[18] S. Treppendhal, P. Jakobsen, Acta Chem. Scand. Ser B, B32 (1978) 697.
[19] S.H. Jung, J.H. Ahn, S.K. Park, J.K. Choi, Bull. Chem. Soc. 23 (2002) 149.
[20] A. Khoramabadi-zad, H. Veisi, S.A. Akbari, A. Shiri, J. Chin. Chem. Soc. 54 (2007) 499.
[21] K. Ishihara, M. Kubota, H. Yamamoto, Synlett (1996) 265.
[22] J. Izumi, I. Shiina, T. Mukaiyama, Chem. Lett. (1995) 141.
[23] R. Kumareswaran, A. Gupta, Y.D. Vankar, Synth. Commun. 27 (1997) 227.
[24] T. Okano, K. Miyamoto, Kiji, J. Chem. Lett. (1995) 246.
[25] J. Iqbal, R.R. Srivastava, J. Org. Chem. 57 (1992) 2001.
[26] T. Mukaiyama, I. Shiina, M. Miyashita, Chem. Lett. (1992) 625.
[27] M. Miyashita, I. Shiina, T. Mukaiyama, Bull. Chem. Soc. Jpn. 66 (1993) 1516.
[28] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Chem. Commun. (2003) 764.
[29] M. Habibi, S. Tangestaninejad, V. Mirkhani, B. Yadollahi, Tetrahedron 57 (2001) 8333.
[30] N. Iranpoor, H. Firouzabadi, A. Jamalian, Tetrahedron Lett. 46 (2005) 7963.
[31] H. Hagiwara, K. Morohashi, H. Sakai, T. Suzuki, M. Ando, Tetrahedron (1998) 5845.
[32] R.N. Ram, N.K. Meher, Tetrahedron 58 (2002) 2997.
[33] M. Hosseini-Sarvari, H. Sharghi, J. Org. Chem. 71 (2006) 6652.
[34] R. Ghorbani-Vaghei, M.A. Zolfigol, M. Chegeny, H. Veisi, Tetrahedron Lett. 47 (2006) 4505.
[35] R. Ghorbani-Vaghei, H. Jalili, Synthesis 7 (2005)1099.
[36] R. Ghorbani-Vaghei, E. Shahbazee, J. Braz. Chem. Soc. 16 (2005) 647.
[37] M.A. Zolfigol, R. Ghorbani-Vaghei, S. Mallakpour, G. Chehardoli, A. Ghorbani Choghamani, A. Yazdi Hosain, Synthesis 10 (2006) 1631.
[38] R. Ghorbani-Vaghei, H. Jalili, E. Shahbazee, H. Veisi, J. Chin. Chem. Soc. 53 (2006) 2.
[39] R. Ghorbani-Vaghei, E. Shahbazee, H. Veisi, Mendeleev Commun. (2005) 207.
[40] E. Kolvari, A. Ghorbani-Choghamarani, P. Salehi, F. Shirini, M.A. Zolfigol, J. Iran. Chem. Soc. 4 (2007) 126.