Heteroatom Chemistry
Volume 26, Number 6, 2015

Hydrolysis of Diazonium Salts Using a Two-Phase System (CPME and Water)

Toshihide Taniguchi,[1,2] Mitsutaka Imoto,[1] Motonori Takeda,[1] Takeo Nakai,[3] Masatoshi Mihara,[3] Toshiyuki Iwai,[3] Takatoshi Ito,[3] Takumi Mizuno,[3] Akihiro Nomoto,[2] and Akiya Ogawa[2]

[1]*Seika Corporation, Wakayama, 641-0007, Japan*

[2]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, 599-8531, Japan*

[3]*Osaka Municipal Technical Research Institute, Joto-ku, Osaka, 536–8553, Japan*

Received 23 April 2015; revised 26 May 2015

ABSTRACT: *A new method for the hydrolysis of diazonium salts, without the formation of tar, was developed. A two-phase system consisting of cyclopentyl methyl ether (CPME) and water is very effective for the hydrolysis of diazonium salts. Using this solvent system, the diazonium salt prepared from 3-(4-nitrophenoxy)aniline gave 3-(4-nitrophenoxy)phenol in high yield (96%) within 20 min. The synthesized phenol is an industrially important raw material in polymer syntheses. Furthermore, the use of the present two-phase system of CPME and water successfully brought about the efficient conversions of several m-substituted anilines into the corresponding m-substituted phenols. This is the first example of hydrolysis of diazonium salts using the two-phase system (CPME and water).* © 2015 Wiley Periodicals, Inc. Heteroatom Chem. 26:411–416, 2015; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21275

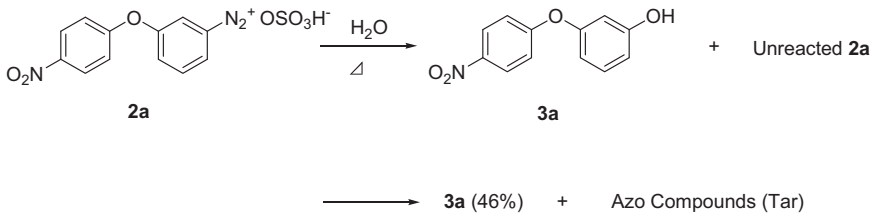
INTRODUCTION

Phenoxyphenols play a key role in the field of aromatic polymer materials. In particular, 3-phenoxyphenols and 4-phenoxyphenols have received much attention as monomers of polyphenylene oxide because they are more reactive than unsubstituted phenol, and less isomer formation occurs during the coupling reaction [1, 2].

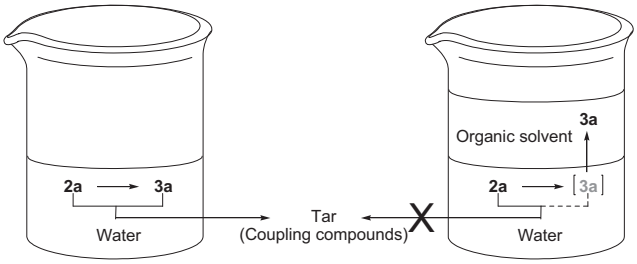
In our project concerning the production of a raw material for functional plastics (polyimide resin), 3-(4-aminophenoxy)phenol and 3-(4-nitrophenoxy)phenol (**3a**) are very significant compounds [3, 4]. Thus, many synthetic methods for **3a** have been reported. Among them, **3a** has typically been synthesized through the aromatic nucleophilic substitution of resorcinol with 4-halogenated nitrobenzenes [5]. However, this reaction required high temperature and prolonged reaction time, and the yields were moderate. Generally, the synthesis of 3-substituted phenols is difficult, because phenol has ortho-/para-directing property due to the electron-donating hydroxyl group. For ortho- and para-functionalization of phenols, many methodologies are well investigated. However, this strong directing effect prevents the selective direct functionalization of phenols at the meta position [6].

To develop a safe, simple, low-cost, and high-yielding synthetic method, the synthesis of **3a** using the hydrolysis of diazonium salt **2a** prepared from 3-(4-nitrophenoxy)aniline (**1a**) was examined [7]. However, the classical reactions described in textbooks are not always practical and industrially feasible. In such reaction systems, large amounts of tar

Correspondence to: Toshihide Taniguchi; e-mail: t-taniguchi@waseika.com.



SCHEME 1 Synthesis of **3a**.



SCHEME 2 Expected effect of two-phase system.

are formed during the reaction, making the reasonable access of suitable experimental manipulation difficult. To solve this problem, the use of a two-phase system comprising a mixture of an organic solvent and water was envisioned. After intensive examinations of the hydrolysis of **2a** prepared from **1a** using a variety of two-phase systems, we herein report the surprising effect of a two-phase system consisting of cyclopentyl methyl ether (CPME) and water. To the best of our knowledge, this is the first example of the hydrolysis of diazonium salts using the two-phase system.

RESULTS AND DISCUSSION

At the outset, we attempted to synthesize **3a** according to a literature method [7] (Scheme 1). The diazonium salts **2a**, which was prepared from **1a** using sodium nitrite and sulfuric acid, was poured into a dilute solution of sulfuric acid under heating at reflux temperature. In this hydrolysis procedure, tar was formed, and the yield of **3a** was 46% (Scheme 1). In thin layer chromatography analysis, many polar compounds were observed. The tar formation suggested that a competitive reaction of **3a** with unreacted **2a** occurred in the aqueous phase. In other words, the tar polymer or oligomer may be formed via diazo coupling of the diazonium salt **2a** with the resulting phenol **3a** before the nucleophilic substitution of **3a** with water takes place.

To prevent the diazo coupling reaction, a two-phase system of organic solvent and water was devised (Scheme 2 and Table 1). Diazonium salt **2a**, formed in the aqueous phase, is converted into **3a**, which is immediately extracted by organic solvent. Using this two-phase system (organic solvent and water), it is possible to avoid the diazo coupling reaction between the diazonium salt **2a** and obtained **3a**.

Diazonium salt **2a** was prepared from **1a** and sodium nitrite in concentrated sulfuric acid. The solution of **2a** was poured into a mixture of an organic solvent and water, and then the resulting solution was refluxed (Method A, see Experimental section).

The hydrolysis reaction using toluene as a cosolvent gave **3a** in low yield (26%) (Entry 1). As toluene has an electron-donating Me group, it can act as a good coupler for the diazo coupling reaction. Therefore, it was considered that the diazo coupling reaction of **2a** with toluene proceeded preferentially. Next, using ethyl acetate, the yield of **3a** improved to 67% (Entry 2). In the case of ethyl acetate, the two-phase system was maintained at the initial stage, but became monophasic at the end of the hydrolysis reaction. This is because of the hydrolysis of ethyl acetate with sulfuric acid, which affords acetic acid and ethanol. Keeping the good result of ethyl acetate (Entry 2) in mind, tolerance of several esters under the strong acidic conditions was examined (Entries 3–6). Butyl acetate and *s*-butyl acetate gave **3a** in high yields (Entries 4 and 5). After the reaction, however, acetic acid was formed. Chlorinated solvents and nitrobenzene were also examined. In these cases, tar was formed and **3a** was produced in moderate yields (64–71%) (Entries 7–11). In the hydrolysis of **2a** with water, product **3a** and tar tend to float at the surface of water. Hence, the extractive effect for **3a** with heavier solvents such as chlorinated solvents might be lower than that in lighter solvents. Also, chlorinated solvents are industrially less accessible. Ketones were also examined as cosolvents. The hydrolysis of **2a** proceeded with excellent yields in ketones (88–89%) (Entries 12–14). However, a highly unpleasant odor was occasionally generated as a result of oxidation of the ketones. Therefore, ketones are not suitable as cosolvents for the industrial production of phenols **3**. Then, the effect of ethers was examined (Entries 15–17). To our surprise, the

TABLE 1 Optimization of Organic Solvents for the Two-Phase System

Entry	*Solvent*	*Yield (%)*[a]	*Entry*	*Solvent*	*Yield (%)*[a]
1	Toluene	26[b]	13	Methyl isobutyl ketone	89
2	Ethyl acetate	67[b]	14	Diisobutyl ketone	88
3	Isopropyl acetate	78	15	2-Methy itetra hydrofuran	77[b]
4	Butyl acetate	84	16	Methyl f-butyl ether	64
5	s-Butyl acetate	85	17	Cyclopentyl methyl ether (CPME)	96[b]
6	f-Butyl acetate	62	18	Methyl alcohol	63
7	Chloroform	64[b]	19	Acetonitrile	60
8	1,2-Dichloroethane	64	20	Isopropyl alcohol	66
9	Chlorobenzene	68	21	f-Butyl alcohol	70
10	1,2-Dichlorobenzene	70	22	Sulfolane	71
11	Nitrobenzene	71	23	Tetrahydrofuran	80[b]
12	2-Pentanone	88			

[a]HPLC yields.
[b]Isolated yields.

reaction using CPME proceeded smoothly to give **3a** in almost quantitative yield (Entry 17). In diazotizations, few examples using a mixture of an organic solvent and water have been reported [8, 9]. However, this is the first example of the hydrolysis of diazonium salts **2** in two-phase system (CPME and water).

Finally, solvents that are miscible with water were investigated (Entries 18–23). The formation of **3a** in moderate yields (60–80%) was observed. However, tar was also formed in these reactions. The use of immiscible organic solvents with water is more effective for selective synthesis of **3a** than that of miscible solvents.

These results suggest that the ideal organic solvent for the two-phase system is immiscible with water, acid resistant, and lighter than water. CPME is the best cosolvent for this two-phase system. CPME has recently received much attention because of high boiling point (106°C), resistance to peroxide formation, extremely easy dehydration, and high solubility with organic compounds. Also, CPME is applicable for a variety of synthetic methods using organolithium reagents, Grignard reactions, and various cross-coupling reactions in the presence of Pd catalysts [10–17].

With the optimized reaction conditions in hand, the scope and limitations of the syntheses of various phenols (**3a**–**3j**) from anilines (**1a**--**1j**) through the hydrolyses of diazonium salt (**2a**–**2j**) using method A (see Scheme 2) or method B were examined. In method B, the syntheses of diazonium salts **2** were performed by reacting anilines **1** with sodium nitrite in sulfuric acid and CPME (see Experimental section). The results are shown in Table 2. The meta-substituted phenoxyanilines (**1a** and **1b**) gave **3a** and **3b** in almost quantitative yields (Entries 1 and 2). However in the case of benzyloxyaniline (**1c**), **3c** was obtained in moderate yield (64%) (Entry 3). The anilines featuring meta-substituted electron-donating group (**1d**–**1f**) and meta-substituted electron-withdrawing group (**1g**, **1i**, and **1j**) afforded the corresponding phenols (**3d**–**3g**, **3i**, and **3j**) in excellent yields (91–98%) (Entries 4–7, 9, and 10). For the synthesis of *m*-nitrophenol (**3h**), higher reaction temperature was required and the yield of **3h** was lowered. Then, the use of pseudocumene (bp 169°C) as a cosolvent afforded **3h** in reasonable yield (Entry 8). These results show that a simple and useful synthetic method for *m*-substituted phenols was established successfully.

Furthermore, the syntheses of ortho- and para-substituted phenols **3k**–**3n** from the anilines **1k**–**1n** were investigated (Table 3). The corresponding products **3k**–**3n** were obtained in high yields (82–96%) (Entries 1–4). Also, aniline (**1o**) was smoothly converted into phenol (**3o**) in 93% yield (Entry 5). Finally, 3-aminopyridine (**1p**) was converted into 3-hydroxypyridine (**3p**) quantitatively (Entry 6).

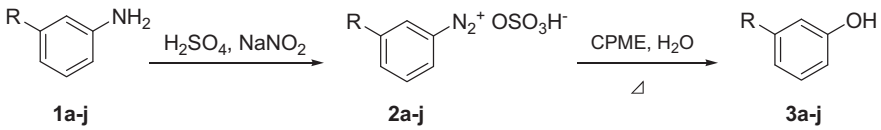
CONCLUSIONS

In summary, a useful synthetic method for various phenols **3** without the formation of tar was developed. The hydrolysis of diazonium salts **2** prepared from anilines **1** gave **3** in good to excellent yields using the two-phase system of CPME and water. From the practical and industrial viewpoints, the present method for producing a variety of phenols **3** is very noteworthy because of the use of easily available and cheap reagents and solvents, and mild reaction conditions.

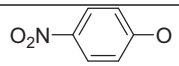
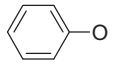
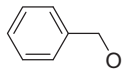
EXPERIMENTAL

Melting points were determined with a YAMATO MP-21 instrument (Yamato Scientific Co., Ltd.,

TABLE 2 Synthesis of m-Substituted Phenols (**3a–j**) in the Two-Phase System (CPME and Water)

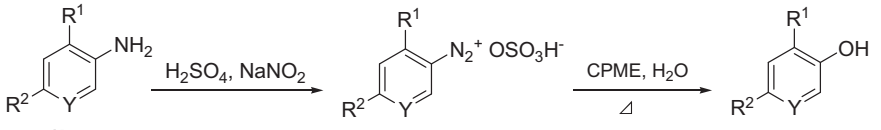


1a-j **2a-j** **3a-j**

Entry	*R*	*Product*	*Yield (%)*[a]	*Method*
1		**3a**	96	A
2		**3b**	95	B
3		**3c**	64	B
4	*i*-Pr	**3d**	96	B
5	Me	**3e**	93	B
6	MeO	**3f**	91	B
7	Ac	**3g**	92	B
8	$N0_2$	**3h**	56, 75[b]	B
9	CF_3	**3i**	94	A
10	COOH	**3j**	98	A

[a]Isolated yields.
[b]Cosolvent is pseudocumene.

TABLE 3 Synthesis of **3k–p** in the Two-Phase System (CPME and Water)



1k-p **2k-p** **3k-p**

Entry	*R^1*	*R^2*	*Y*	*Product*	*Yield (%)*[a]
1	Me	H	CH	**3k**	83
2	COOH	H	CH	**31**	89
3	H	Me	CH	**3m**	82
4	H	COOH	CH	**3n**	96
5	H	H	CH	**3o**	93
6	H	H	N	**3p**	100

[a]Method B was used. Isolated yields.

Tokyo, Japan) and were uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on JEOL JNM-AL300 (300 MHz, 75 MHz) and JEOL JNM-ECX400 (400 MHz, 100 MHz) instruments (JEOL Ltd., Tokyo, Japan). Mass spectra were measured on GC-MS Varian 3400 with Varian SATURN 2000 (Agilent Technologies, Inc., Santa Clara, USA) and Shimadzu LCMS-2020 featuring a DART (Direct Analysis Real Time) source (SHIMADZU CORPORATION, Kyoto, Japan).

*General Procedure for the Synthesis of Phenols **3***

Method A. Into the concentrated sulfuric acid (8.0 mL), aniline **1** (5.0 mmol) was added carefully. A mixture of **1** and sulfuric acid was cooled with an ice bath with stirring. To the yellow or colorless solution, sodium nitrite (0.38 g, 5.5 mmol) was added at 5°C. The solution was warmed to room temperature and stirred for additional 1 h to produce diazonium salt **2**. Next, the diazonium salt solution was poured into another flask containing water (40 mL) and CPME (35 mL) with stirring. The mixture was refluxed for 15–20 min. After the reaction, the product was extracted with AcOEt and dried over $MgSO_4$. After evaporation of organic solvents, product **3** was obtained by purification using silica gel column chromatography.

Method B. To a mixture of ice (26 g) and concentrated sulfuric acid (8.0 mL), aniline (5.0 mmol) was added slowly and stirred for several minutes at room temperature. CPME (35 mL) was added to the solution. An aqueous solution (14 mL) of sodium nitrite (0.38 g, 5.5 mmol) was added dropwise over 10 min, and the mixture was refluxed for 15–20 min. After completion of the reaction, the resulting solution was allowed to cool to room temperature, and

then extracted with AcOEt and dried over $MgSO_4$. After purification by silica gel column chromatography, phenol **3** was obtained.

3-(4-Nitrophenoxy)phenol **(3a)**. Yield 1.110 g (96%), mp 95–96°C (Lit. [18] 96–97°C). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.26 (s, 1H, OH), 6.59 (t, J = 2.4 Hz, 1H), 6.65 (ddd, J = 8.2, 2.4, 0.8 Hz, 1H), 6.72 (ddd, J = 8.2, 2.4, 0.8 Hz, 1H), 7.04 (dt, J = 9.2, 2.1 Hz, 2H), 7.27 (t, J = 8.2 Hz, 1H), 8.20 (dt, J = 9.2, 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 108.0, 112.6, 112.7, 117.4, 126.1, 131.1, 142.7, 155.9, 157.4, 163.2. MS (EI) *m/z* (%): 231 (M^+, 100), 207 (24), 128 (52), 65 (82).

3-Phenoxyphenol **(3b)**. Yield 0.882 g (95%), oil (Lit. [19]). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.84 (s, 1H, OH), 6.48 (t, J = 2.4 Hz, 1H), 6.56 (dd, J = 8.2, 2.4, 1H), 6.58 (dd, J = 8.2, 2.4 Hz, 1H), 7.03 (d, J = 7.3 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 7.17 (t, J = 8.2 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 106.0, 110.2, 111.1, 119.4, 123.7, 129.9, 130.5, 156.8, 156.9, 158.8. MS (EI) *m/z* (%): 186 (M^+, 100), 157 (21), 129 (27), 77 (35), 51 (94).

3-Benzyloxyphenol **(3c)**. Yield 0.643 g (64%), mp 49–50°C (Lit. [20] 50–51°C). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.71 (s, 1H, OH), 5.04 (s, 2H, CH_2), 6.44 (ddd, J = 8.2, 2.4, 0.9, 1H), 6.48 (t, J = 2.4 Hz, 1H), 6.57 (ddd, J = 8.2, 2.4, 0.9 Hz, 1H), 7.14 (t, J = 8.2 Hz, 1H), 7.33–7.44 (m, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 70.1, 102.6, 107.5, 108.2, 127.6, 128.1, 128.7, 130.3, 136.9, 156.7, 160.2. MS (EI) *m/z* (%): 200 (M^+, 11), 91 (100), 65 (15), 51 (6).

3-Isopropylphenol **(3d)**. Yield 0.652 g (96%), oil (Lit. [21]). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.23 (d, J = 6.9 Hz, 6H, CH_3), 2.86 (sep, J = 6.9 Hz, 1H, CH), 4.76 (s, 1H, OH), 6.65 (ddd, J = 7.7, 2.2, 0.9 Hz, 1H), 6.71 (t, J = 2.2 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.0, 34.1, 112.7, 113.4, 119.1, 129.5, 151.1, 155.6. MS (EI) *m/z* (%): 136 (M^+, 38), 121 (100), 103 (15), 91 (23), 77 (24), 65 (11), 51 (15), 41 (21).

m-Cresol **(3e)**. Yield 0.504 g (93%), oil (Lit. [22]). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.30 (s, 3H, CH_3), 4.78 (s, 1H, OH), 6.62–6.66 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.4, 112.4, 116.2, 121.8, 129.6, 140.0, 155.4. MS (EI) *m/z* (%): 108 (M^+, 100), 107 (97), 90 (17), 79 (41), 51 (35), 40 (21).

3-Methoxyphenol **(3f)**. Yield 0.565g (91%), oil (Lit. [23]). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.77 (s, 3H, CH_3), 5.15 (s, 1H, OH), 6.41–6.44 (m, 2H), 6.50 (ddd, J = 8.1, 2.3, 0.9 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 55.4, 101.7, 106.6, 108.0, 130.3, 156.8, 160.9. MS (EI) *m/z* (%): 124 (M^+, 100), 94 (61), 81 (33), 66 (33), 53 (62), 41 (18).

3-Acetylphenol **(3g)**. Yield 0.629 g (92%), mp 95–96°C (Lit. [24] 96°C). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.61 (s, 3H, CH_3), 6.85 (s, 1H, OH), 7.12 (ddd, J = 8.0, 2.7, 0.9 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.51 (dt, J = 8.0, 0.9 Hz, 1H), 7.55–7.56 (m, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 26.9, 114.8, 121.0, 121.2, 130.0, 138.4, 156.5, 199.5. MS (EI) *m/z* (%): 136 (M^+, 62), 121 (91), 93 (65), 65 (49), 43 (100).

3-Nitrophenol **(3h)**. Yield 0.519 g (75%), mp 95–96°C (Lit. [7] 95–96°C). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.39 (s, 1H, OH), 7.18 (ddd, J = 8.2, 2.3, 0.9 Hz, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.70 (t, J = 2.3 Hz, 1H), 7.82 (ddd, J = 8.2, 2.3, 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 110.6, 116.0, 122.1, 130.4, 149.2, 156.3. MS (EI) *m/z* (%): 139 (M^+, 70), 93 (42), 81 (24), 65 (100), 53 (40).

3-Trifluoromethylphenol **(3i)**. Yield 0.760 g (94%), oil (Lit. [25]). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.04 (s, 1H, OH), 7.01 (dd, J = 2.3, 8.2 Hz, 1H), 7.08 (s, 1H), 7.20 (dd, J = 8.2, 2.3 Hz, 1H), 7.36 (t, J = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 112.5 (q, J = 3.7 Hz), 117.8, (q, J = 3.7 Hz), 119.0, 124.0 (q, J = 274 Hz), 130.4, 132.3 (q, J = 33 Hz), 155.8. MS (EI) *m/z* (%): 162 (M^+, 100), 143 (33), 112 (24), 63 (18).

3-Hydroxybenzoic acid **(3j)**. Yield 0.678 g (98%), mp 197–198°C (Lit. [26] 199–200°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.01 (ddd, J = 7.9, 2.4, 1.2 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.35 (t, J = 2.4 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 9.77 (s, 1H, OH), 12.8 (brs, 1H, COOH). ^{13}C NMR (DMSO-d_6) δ (ppm): 116.3, 120.4, 120.5, 130.1, 132.5, 157.9, 167.8. MS (Neg-DART) *m/z*: 137 ([M – H]$^-$).

o-Cresol **(3k)**. Yield 0.449 g (83%), oil (Lit. [22]). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.25 (s, 3H, CH_3), 4.72 (s, 1H, OH), 6.76 (d, J = 7.7 Hz, 1H), 6.85 (td, J = 7.7, 1.2 Hz, 1H), 7.06–7.13 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.9, 115.0, 120.9, 123.9, 127.3, 131.2, 153.8. MS (EI) *m/z* (%): 108 (M^+, 100), 107 (83), 90 (25), 79 (42), 51 (45), 40 (12).

Salicylic acid **(3l)**. Yield 0.614 g (89%), mp 157.5–158.5°C (Lit. [27] 157.5–158°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.92 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 7.51 (td, J = 7.6, 0.6 Hz, 1H), 7.79 (dd, J = 7.6, 1.6 Hz, 1H), 11.50 (brs, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 113.5, 117.6, 119.7, 130.8,

136.2, 161.7, 172.5. MS (Neg-DART) *m/z*: 137 ([M – H]$^-$).

p-Cresol **(3m)**. Yield 0.444 g (82%), oil (Lit. [22]). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.27 (s, 3H, CH_3), 4.75 (s, 1H, OH), 6.73 (dd, J = 8.2, 2.0 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 20.6, 115.2, 130.2, 153.2. MS (EI) *m/z* (%): 108 (M$^+$, 94), 107 (100), 90 (12), 77 (33), 51 (42), 40 (11).

4-Hydroxybenzoic acid **(3n)**. Yield 0.660 g (96%), mp 209.5–210.5°C (Lit. [28] 210–211°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.82 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 10.2 (brs, 1H, OH), 12.4 (brs, 1H, COOH). ^{13}C NMR (DMSO-d_6) δ (ppm): 115.6, 121.9, 132.1, 162.1, 167.7. MS (Neg-DART) *m/z*: 137 ([M – H]$^-$).

Phenol **(3o)**. Yield 0.435 g (93%), mp 40.5–41.5°C (Lit. [29] 41–43°C). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.82 (s, 1H, OH), 6.81–6.85 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 7.22–7.27 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 115.4, 120.9, 129.8, 155.5. MS (EI) *m/z* (%): 94 (M$^+$, 100), 66 (39), 55 (18), 40 (39).

3-Hydroxypyridine **(3p)**. Yield 0.479 g (100%), mp 126–127°C (Lit. [30] 127°C). ^{1}H NMR (Acetone-d_6) δ (ppm): 7.20 (t, J = 2.1 Hz, 2H), 8.08 (t, J = 3.2 Hz, 1H), 8.21 (t, J = 1.6 Hz, 1H), 8.92 (brs, 1H, OH). ^{13}C NMR (Acetone-d_6): δ (ppm) 121.9, 124.0, 138.1, 140.9, 153.7. MS (EI) *m/z* (%): 95 (M$^+$, 100), 67 (24), 40 (79).

REFERENCES

[1] Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Kubota, M.; Shiga, A.; Terahara, A.; Uyama, H.; Kobayashi, S. J Am Chem Soc 1998, 120, 8529–8530.
[2] Kobayashi, S.; Higashimura, H. Prog Polym Sci 2003, 28, 1015–1048.
[3] Shimada, K. Jpn Kokai Tokkyo Koho 1994, 219999.
[4] Shimada, K. Jpn Kokai Tokkyo Koho 1994, 293720.
[5] Xie, C.; Sullivan, K. A.; Laurila, M. E.; Mitchell, D. N.; Pu, Y. J Synth Commun 2007, 38, 21–32.
[6] Luo, J.; Preciado, S.; Larrosa, I. J Am Chem Soc 2014, 136, 4109–4112.
[7] Manske, R. H. F. Org Synth Coll 1941, 1, 404–406.
[8] Yamashita, T.; Kawai, N.; Tokuyama, H.; Fukuyama, T. J Am Chem Soc 2005, 127, 15038–15039.
[9] Tokukura, Y.; Nagatomi, T. Jpn Kokai Tokkyo Koho 2000, 53626.
[10] Watanabe, K.; Goto, K. J Synth Org Chem Jpn 2003, 61, 806–808.
[11] Watanabe, K.; Yamagiwa, N.; Torisawa, Y. Org Process Res Dev 2007, 11, 251–258.
[12] Watanabe, K. Molecules 2013, 18, 3184–3194.
[13] Antonucci, V.; Coleman, J.; Ferry, J. B.; Johnson, N.; Mathe, M.; Scott, J. P.; Xu, J. Org Process Res Dev 2011, 15, 939–941.
[14] Kobayashi, S.; Kuroda, H.; Ohtsuka, Y.; Kashihara, T.; Masuyama, A.; Watanabe, K. Tetrahedron 2013, 69, 2251–2259.
[15] Okabayashi, T.; Iida, A.; Takai, K.; Nawate, Y.; Misaki, T.; Tanabe, Y. J Org Chem 2007, 72, 8142–8145.
[16] Shimada, T.; Suda, M.; Nagano, T.; Kakiuchi, K. J Org Chem 2005, 70, 10178–10181.
[17] Roche, M.; Bignon, J.; Brion, J.-D.; Hamze, A.; Alami, M. J Org Chem 2014, 79, 7583−7592.
[18] Ikawa, K. Yakugaku Zasshi 1959, 79, 1498–1502.
[19] Sax, K. J.; Saari, W. S.; Mahoney, C. L.; Gordon, J. M. J Org Chem 1960, 25, 1590–1595.
[20] Fitton, A. O.; Ramage, G. R. J Chem Soc 1962, 4870–4874.
[21] Joshi-Pangu, A.; Ganesh, M.; Biscoe, M. R. Org Lett 2011, 13, 1218–1221.
[22] Kendall, J.; Beaver, J. J. J Am Chem Soc 1921, 43, 1853–1867.
[23] Thakur, K. G.; Sekar, G. Chem Commun 2011, 47, 6692–6694.
[24] Gogoi, P.; Sarmah, G. K.; Konwar, D. J Org Chem 2004, 69, 5153–5154.
[25] Chatterjee, N.; Chowdhury, H.; Sneh, K.; Goswami, A. Tetrahedron Lett 2015, 56, 172–174.
[26] Ungnade, H. E.; Henick, A. S. J Am Chem Soc 1942, 64, 1737–1738.
[27] Hauptschein, M.; Saggiomo, A. J.; Stokes, C. S. J Am Chem Soc 1955, 77, 2284–2287.
[28] Kikuchi, M.; Sato, K.; Shiraishi, Y.; Nakayama, R.; Watanabe, R.; Sugiyama, M. Yakugaku Zasshi 1990, 110, 354–357.
[29] Molander, G. A.; Cavalcanti, L. N. J Org Chem 2011, 76, 623–630.
[30] Anderso, K. W.; Ikawa, T.; Tundel, R. E.; Buchwald, S. L. J Am Chem Soc 2006, 128, 10694–10695.