A New Method of Synthesizing Deoxybenzoins from 1,3-Dimethyl-2-(α-benzyloxybenzyl)imidazolium and 1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodides Based on Wittig-Type Rearrangement[1)]

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The treatment of 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium iodides 1 with a base gave deoxybenzoins 2 in moderate yields. Sodium hydride (NaH), potassium carbonate (K_2CO_3), and cesium carbonate (Cs_2CO_3) were effective bases in this reaction. Deoxybenzoins 2 were produced through rearrangement of the benzyl group followed by expulsion of the 1,3-dimethylbenzimidazolium ylide (A). The rearrangement proceeds in a way similar to Wittig rearrangement. Deoxybenzoins 2 were also formed in good yields from 1,3-dimethyl-2-(α-benzyloxybenzyl)-imidazolium iodides 4 upon similar treatment. However, the quaternary salts having a thiazolium moiety 5a and a pyridinium moiety 6a failed to produce deoxybenzoin (2a).

Key words deoxybenzoin; 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium salt; Wittig rearrangement; metal carbonate; azolium ylide; azolium salt

In benzoin condensation and related reactions, we have shown that the chemical behavior of azolium ylide is similar to, but not identical with, that of cyanide ion.[2)] It is therefore of interest to examine the effects of azolium ylide or azolium salts in other cyanide ion- or cyano group-promoted reactions.

Wittig rearrangement[3)] is a well known anion rearrangement, like the Stevens[4)] and Sommelet–Hauser[5)] rearrangements. Cast *et al.* reported that the treatment of several ethers with base gave alcohols.[6)] Among the ethers that they used, benzyl α-cyanobenzyl ether (**3**) unexpectedly gave deoxybenzoin (**2a**) in a low yield. They suggested that **2a** was produced by rearrangement of the benzyl group followed by expulsion of cyanide ion.

On the basis of the chemical similarities between the cyano group and azolium salts, we considered that 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium iodide (**1a**) corresponds to benzyl α-cyanobenzyl ether (**3**), and thus deoxybenzoin (**2a**) might be formed when compound **1a** is treated with base in a way similar to that in the above reaction. In the previous communication, we confirmed that this is the case.[1)] We now wish to report the results in detail as a new method of synthesizing deoxybenzoins **2** from 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium iodides **1** or 1,3-dimethyl-2-(α-benzyloxybenzyl)imidazolium iodides **4**. Deoxybenzoins **2** are generally used as starting compounds for syntheses of isoflavones and chalcones.[7)]

When the benzimidazolium salt **1a** was treated with sodium hydride (NaH) in tetrahydrofuran (THF), deoxybenzoin (**2a**) was produced in 57% yield, as expected. Several other bases, such as potassium carbonate (K_2CO_3) and cesium carbonate (Cs_2CO_3), were also effective. Among several metal carbonates, such as sodium carbonate (Na_2CO_3), K_2CO_3, rubidium carbonate (Rb_2CO_3), and Cs_2CO_3, which are considered weak bases, Cs_2CO_3 was most effective. The reasons for this might be its solubility and the stabilizing effect of the released benzyl anion. In this reaction, THF or *N*,*N*-dimethylformamide (DMF) could be used as the solvent. Further experiments were carried out using metal carbonates as bases.

To examine the scope of this reaction, several 1,3-dimethyl-2-(α-benzyloxybenzyl)-benzimidazolium iodides **1** were prepared, and treated with K_2CO_3 in DMF. As shown in Chart 3, the expected deoxybenzoins **2** were formed in moderate yields.

This reaction was also applied to other azolium salts. An attempt to produce acetophenone (**2m**) from 1,3-dimethyl-2-(α-methoxybenzyl)benzimidazolium iodide

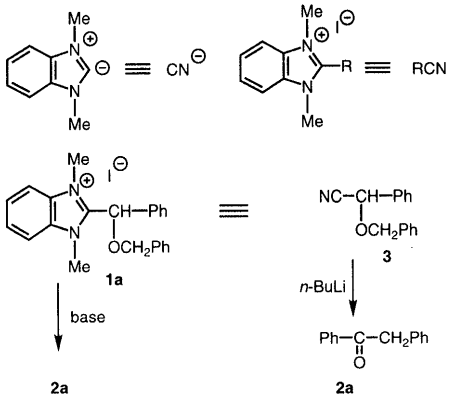
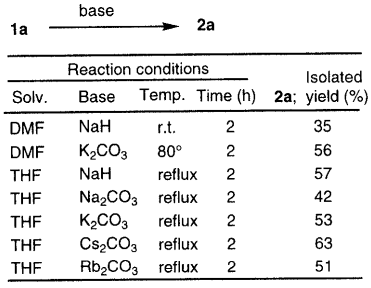


Chart 1



Reaction conditions				Isolated
Solv.	Base	Temp.	Time (h)	2a; yield (%)
DMF	NaH	r.t.	2	35
DMF	K_2CO_3	80°	2	56
THF	NaH	reflux	2	57
THF	Na_2CO_3	reflux	2	42
THF	K_2CO_3	reflux	2	53
THF	Cs_2CO_3	reflux	2	63
THF	Rb_2CO_3	reflux	2	51

Chart 2

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(**1m**) failed, as had been found in the case of the cyano group.[6]

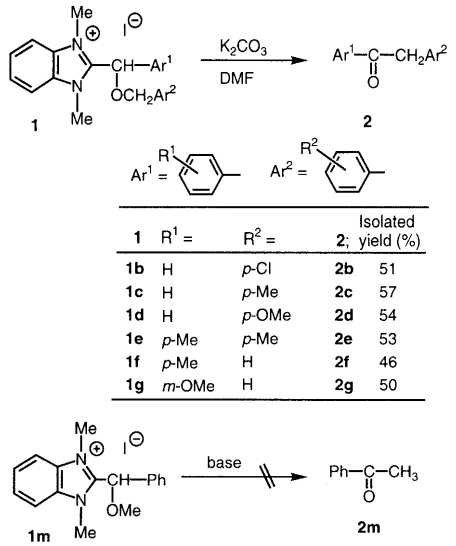
We have already reported that the chemical behavior of imidazolium salts is similar to that of benzimidazolium salts in the benzoin condensation and related reactions.[2] This led us to examine the synthesis of deoxybenzoins **2** by the use of imidazolium salts **4**. When 1,3-dimethyl-2-(α-benzyloxybenzyl)imidazolium iodide (**4a**) was treated with Cs_2CO_3 in THF for 3 h, deoxybenzoin (**2a**) was formed in 63% yield, as expected. As shown in Chart 4, several deoxybenzoins **2** were obtained in good yields from the corresponding imidazolium salts **4**.

However, the quaternary salts, 3-methyl-2-(α-benzyloxybenzyl)thiazolium iodide (**5a**) and 1-methyl-2-(α-benzyloxybenzyl)pyridinium iodide (**6a**), failed to produce deoxybenzoin (**2a**). Namely, on similar treatment of **5a**, only a 4% yield of deoxybenzoin (**2a**) was obtained. On similar treatment of **6a**, formation of **2a** could be detected, but the amount was too small to permit purification. One of the reasons for the low reactivity of these salts might be the low acidity of the hydrogen of the benzyl group in these salts and the poor leaving ability of the ylide. The stability and reactivity of the quaternary salts and the intermediates may also be important, but the details are not clear yet.

Deoxybenzoins **2** are generally produced by Friedel–Crafts reaction,[8] but deoxybenzoins **2** having an *ortho-para* directing group at the *meta* position of the benzoyl group are difficult to prepare. On the other hand, 3-methoxydeoxybenzoin (**2g**), which has an *ortho-para* directing group at the *meta* position, was easily prepared by our present method in good yield. In addition, several deoxybenzoins (**2h—j**) having a methoxy group at the *meta* position could be synthesized in good yields.

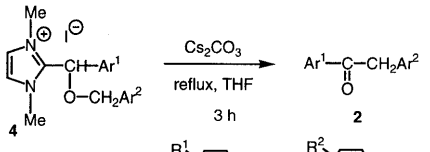
In general, Wittig rearrangement requires a strong base, such as *n*-butyllithium (BuLi), methyllithium (MeLi), or potassium *tert*-butoxide (BuOK), because of the low acidity of the hydrogen of the benzyl group. In contrast, the rearrangement applied to benzimidazolium salts **1** and imidazolium salts **4** proceeded with metal carbonate, because the acidity of the hydrogen of the benzyl group is higher than that of an ordinary benzyl ether owing to the effect of the azolium salts. This result suggested that one of the driving forces of the rearrangement is the formation of the carbanion. In fact, when the rearrangement with K_2CO_3 was applied to 1-methyl-2-(α-benzyloxybenzyl)benzimidazole (**7a**), the reaction did not proceed, because of insufficient acidity of the benzyl group for the removal of hydrogen under this condition. However, the Wittig rearrangement product **10a** was generated in 71% yield by treatment with NaH. The rearrangement product of thiazole, 3-methyl-2-(α-benzyl-α-hydroxybenzyl)thiazole (**11a**), was also formed in 38% yield when the corresponding azole **9a** was treated with NaH. In contrast, similar treatment of imidazole **8a** resulted in recovery of the starting **8a**.

Formation of deoxybenzoins **2** also requires elimination ability of azolium salts or azoles as a leaving group. The rearrangement products of the azoles **10a** and **11a** did not afford deoxybenzoin (**2a**) by release of the azoles, while azolium salts can easily be eliminated as azolium ylides. This result indicates that azolium salts enhance the acidity of the benzyl group at the 2-position, and the azolium ylide generated from an azolium salt acts as a good leaving group. Thus, to produce deoxybenzoins **2** efficiently by



1	R^1 =	R^2 =	2;	Isolated yield (%)
1b	H	*p*-Cl	**2b**	51
1c	H	*p*-Me	**2c**	57
1d	H	*p*-OMe	**2d**	54
1e	*p*-Me	*p*-Me	**2e**	53
1f	*p*-Me	H	**2f**	46
1g	*m*-OMe	H	**2g**	50

Chart 3



4	R^1 =	R^2 =	2;	Isolated yield (%)
4a	H	H	**2a**	63
4b	H	*p*-Cl	**2b**	81
4c	H	*p*-OMe	**2c**	71
4g	*m*-OMe	H	**2g**	79
4h	*m*-OMe	*p*-Cl	**2h**	63
4i	*m*-OMe	*p*-Me	**2i**	88
4j	*m*-OMe	*p*-OMe	**2j**	61
4k	*p*-OMe	H	**2k**	81
4l	*o*-OMe	H	**2l**	76

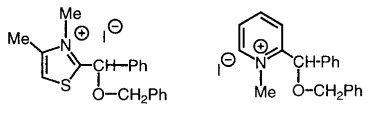


Chart 4

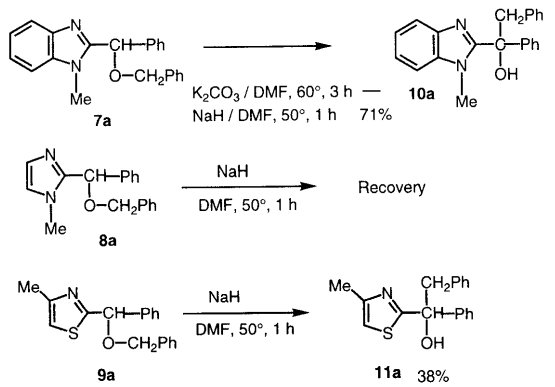


Chart 5

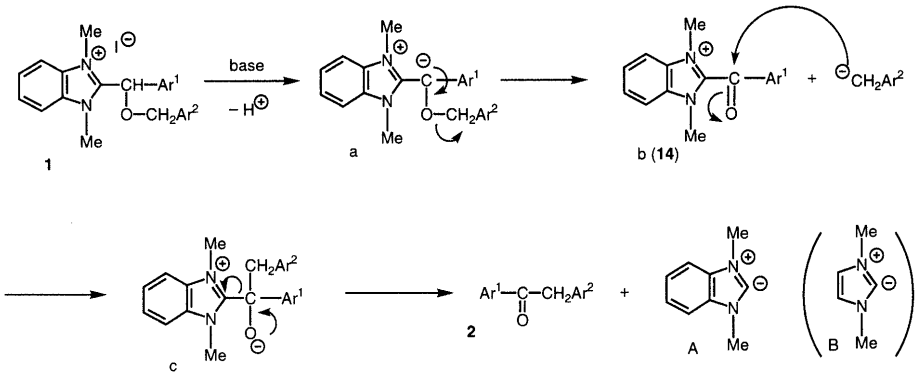


Chart 6

this method, the starting azolium salts must have a strong electron-withdrawing effect, and good leaving ability. Wittig rearrangement of azoles can proceed, but the products cannot furnish the deoxybenzoins **2**. Azolium salts exhibit both effects. Further, benzimidazolium salts **1** and imidazolium salts **4** are able to generate deoxybenzoins **2**.

On the basis of the reaction pathway of benzyl α-cyanobenzyl ether (**3**),[6] the formation pathway of deoxybenzoins **2** from benzimidazolium salts **1** can be considered to be as shown in Chart 6. This pathway involves a 1,2-carbanion shift similar to that in the Wittig rearrangement, which was investigated in detail by Lansbury and Pattison.[9]

To clarify the reaction pathway, cross reaction was carried out. Namely, when the mixture of 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium iodide (**1a**) and 1,3-dimethyl-2-[α-(4-methylbenzyloxy)-4-methylbenzyl]benzimidazolium iodide (**1e**) was treated with Cs_2CO_3 in THF, the expected products, deoxybenzoin (**2a**) and 4,4′-dimethyldeoxybenzoin (**2e**), were formed, together with the unexpected products, 4-methyldeoxybenzoin (**2f**) and 4′-methyldeoxybenzoin (**2c**). The structures were determined on the basis of the retention times compared with those of authentic samples in HPLC. The formation ratio was **2a**:**2c**:**2e**:**2f** = 5:1:5:1. The ratio was determined by integration of the benzyl hydrogen signals in the ^{1}H-NMR spectrum. Furthermore, the cross reaction of **1c** and **1f** resulted in the formation of **2a**, **2c**, **2e**, and **2f** (**2a**:**2c**:**2e**:**2f** = 1:5:1:5). These results imply that the rearrangement proceeds through an intermolecular reaction similar to that of the Wittig rearrangement.

When **1a** was treated with K_2CO_3 in MeOH, only methyl benzoate (**12**) was obtained. This result indicates that the rearrangement of the benzyl group proceeds through the formation of the intermediate b (**14**), and the reaction process is intermolecular. As shown in Chart 7, compound **14** reacted with benzylmagnesium chloride (**13**) to give deoxybenzoin (**2a**) together with **15**, which was formed *via* **2a**. Cross reaction of **14** and **1f** yielded **2a** and **2f**. These results further support the idea that compound **14** and benzyl anion are important intermediates in this reaction.

In the proposed reaction pathway, the formation of deoxybenzoin **2** should require only a catalytic amount of base if the released azolium ylide is also effective as a base. However, the reaction of **1a** using a catalytic amount of Cs_2CO_3 (0.2 mol) gave deoxybenzoin (**2a**) in only 12% yield. This result indicates that for the rearrangement to proceed completely, an equimolar quantity of the base is required in this Wittig-type rearrangement.

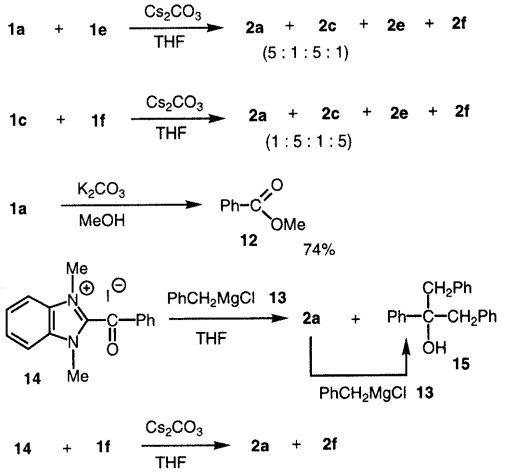


Chart 7

In recent years, it has been considered that the Wittig rearrangement proceeds through a radical mechanism.[10] However, the above results imply that formation of deoxybenzoins **2** from azolium salts proceeds through an anion rearrangement.

The starting azolium salts **1** and **4** were prepared from the corresponding azoles in four steps, involving lithiation of the azole, addition of the arenecarbaldehyde,[11] benzylation, and quaternization. The pyridinium salt **6a** was prepared by reduction of 2-benzoylpyridine (**22**) followed by benzylation and quaternization (Chart 8).

The structures of the newly obtained deoxybenzoins **2** and other compounds described in this paper were supported by spectral data (IR and ^{1}H-NMR), and elemental analyses and/or the mass spectrum. The spectral data are given in the experimental section.

In conclusion, we have found a new method of synthesizing deoxybenzoins **2** by treatment of azolium salts **1** and **4** with base. The reaction proceeds through formation of the carbanion with subsequent benzyl migration in a way similar to the Wittig rearrangement. Elimination of azolium ylide (A or B) affords the deoxybenzoins **2**. The azolium salts **1** and **4** can be easily prepared in comparison to the corresponding cyano compounds. The rearrangement of **1** and **4** proceeds under mild conditions because of the strong electron-accepting effect of the

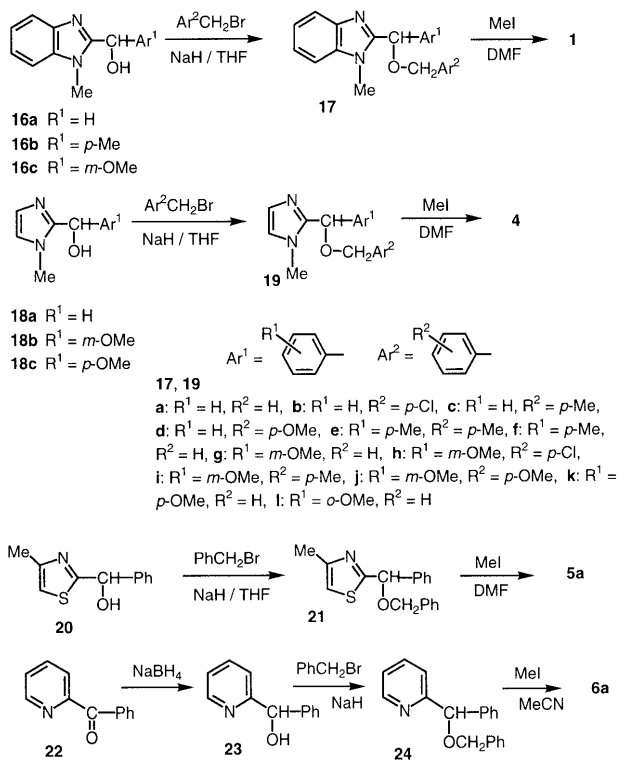


Chart 8

azolium salts. Several deoxybenzoins **2** were synthesized by this method.

Experimental

All melting points are uncorrected. IR spectra were recorded on a JASCO A-102 diffraction grating IR spectrophotometer. ^{1}H-NMR spectra were measured at 60 MHz on a JEOL PMX60SI NMR spectrometer and at 270 MHz on a JEOL JNM-GSX270 FT-NMR spectrometer. Chemical shifts are quoted in parts per million (ppm) with tetramethylsilane as an internal standard, and coupling constants (J) are given in Hz.

Treatment of 1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodide (1a) with Base General Procedure: A mixture of 1,3-dimethyl-2-(α-benzyloxybenzyl)benzimidazolium iodide (**1a**, 1410 mg, 3 mmol) and a base [NaH, 60% in oil, 144 mg (3.6 mmol); K_2CO_3, 455 mg (3.3 mmol); Rb_2CO_3, 762 mg (3.3 mmol); Cs_2CO_3, 1070 mg (3.3 mmol)] in DMF or THF (10 ml) was stirred for 2 h (reaction conditions are shown in Chart 2). The reaction mixture was poured into ice-H_2O and extracted with AcOEt (reaction in DMF) or $CHCl_3$ (reaction in THF). The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt. The first fraction eluted with *n*-hexane–AcOEt (20 : 1) gave deoxybenzoin (**2a**). Colorless scales from *n*-hexane, mp 57—60 °C (lit.,[12] 55—56.5 °C). IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 4.25 (2H, s, CH_2), 7.20—7.61 (8H, m, aromatic H), 7.90—8.15 (2H, m, aromatic H). The results are shown in Chart 2.

When **1a** (1410 mg, 3 mmol) was treated with a catalytic amount of Cs_2CO_3 (214 mg, 0.66 mmol) in refluxing THF for 2 h, **2a** was obtained in 12% yield (71 mg).

Synthesis of Deoxybenzoins 2 from 1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodides 1 General Procedure: A mixture of benzimidazolium salt (**1**, 3 mmol) and K_2CO_3 (455 mg, 3.3 mmol) in 10 ml of DMF was heated at 60 °C for 4 h with stirring. An ice-H_2O mixture was added to the reaction mixture, and the resulting mixture was extracted with AcOEt. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave deoxybenzoin **2**. Yields and reaction conditions are shown in Chart 3.

4′-Chlorodeoxybenzoin (**2b**): Colorless scales (*n*-hexane), mp 137.5—139 °C (lit.,[12] 133 °C). *Anal.* Calcd for $C_{14}H_{11}ClO$: C, 72.89; H, 4.80. Found: C, 72.87; H, 4.91. IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 4.25 (2H, s, CH_2), 7.20—7.68 (7H, m, aromatic H), 7.89—8.13 (2H, m, aromatic H).

4′-Methyldeoxybenzoin (**2c**): Colorless scales (MeOH), mp 97.5—99 °C (lit.,[12] 94—95 °C). *Anal.* Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.87; H, 6.87. IR (KBr) cm^{-1}: 1685 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.30 (3H, s, CH_3), 4.21 (2H, s, CH_2), 7.11—8.10 (9H, m, aromatic H).

4′-Methoxydeoxybenzoin (**2d**): Colorless scales (*n*-hexane), mp 95.5—96 °C (lit.,[12] 98—99 °C). *Anal.* Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23. Found: C, 79.70; H, 6.23. IR (KBr) cm^{-1}: 1690 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, CH_3), 4.22 (2H, s, CH_2), 6.85 (2H, d, J=9 Hz, aromatic H), 7.37—7.63 (3H, m, aromatic H), 7.90—8.11 (2H, m, aromatic H).

4,4′-Dimethyldeoxybenzoin (**2e**): Colorless scales (*n*-hexane), mp 104—105.5 °C (lit.,[12] 97—98 °C). IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.31 (3H, s, CH_3), 2.39 (3H, s, CH_3), 4.21 (2H, s, CH_2), 7.11 (2H, d, J=8 Hz, aromatic H), 7.15 (2H, d, J=8 Hz, aromatic H), 7.24 (2H, d, J=8 Hz, aromatic H), 7.90 (2H, d, J=8 Hz, aromatic H).

4-Methyldeoxybenzoin (**2f**): Colorless scales (*n*-hexane), mp 109.5—110 °C (lit.,[12] 108—109 °C). IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.39 (3H, s, CH_3), 4.25 (2H, s, CH_2), 7.24 (2H, d, J=8 Hz, aromatic H), 7.23—7.33 (5H, m, aromatic H), 7.91 (2H, d, J=9 Hz, aromatic H).

3-Methoxydeoxybenzoin (**2g**): Colorless oil. IR (neat) cm^{-1}: 1682 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.78 (3H, s, OCH_3), 4.23 (2H, s, CH_2), 6.89—7.69 (9H, m, aromatic H). 2,4-Dinitrophenylhydrazone: Orange scales (MeOH), mp 185—187 °C. *Anal.* Calcd for $C_{21}H_{18}N_4O_5$: C, 62.06; H, 4.46; N, 13.79. Found: C, 61.82; H, 4.27; N, 13.60.

Synthesis of Deoxybenzoins 2 from 1,3-Dimethyl-2-(α-benzyloxybenzyl)-imidazolium Iodides 4 General Procedure: A mixture of imidazolium salt (**4**, 3 mmol) and Cs_2CO_3 (1070 mg, 3.3 mmol) in 10 ml of THF was refluxed for 3 h with stirring. An ice-H_2O mixture was added to the reaction mixture, and the resulting mixture was extracted with AcOEt. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with hexane–AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave deoxybenzoin **2**. Yields and reaction conditions are shown in Chart 4.

4′-Chloro-3-methoxydeoxybenzoin (**2h**): Colorless scales (*n*-hexane), mp 49—50 °C. *Anal.* Calcd for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03. Found: C, 69.05; H, 4.84. IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.80 (3H, s, OCH_3), 4.20 (2H, s, CH_2), 6.95—7.67 (8H, m, aromatic H).

3-Methoxy-4′-methyldeoxybenzoin (**2i**): Colorless scales (*n*-hexane), mp 83—84 °C. *Anal.* Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.11; H, 6.65. IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.29 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 4.19 (2H, s, CH_2), 6.90—7.68 (8H, m, aromatic H).

3,4′-Dimethoxydeoxybenzoin (**2j**): Colorless scales (*n*-hexane), mp 59—60 °C. *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.05; H, 6.33. IR (KBr) cm^{-1}: 1682 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.76 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 4.19 (2H, s, CH_2), 6.76—7.71 (8H, m, aromatic H).

4-Methoxydeoxybenzoin (**2k**): Colorless scales (*n*-hexane), mp 77—79 °C. IR (KBr) cm^{-1}: 1673 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.81 (3H, s, OCH_3), 4.29 (2H, s, CH_2), 6.86 (2H, d, J=9 Hz, aromatic H), 7.21 (5H, s, aromatic H), 7.92 (2H, d, J=9 Hz, aromatic H).

2-Methoxydeoxybenzoin (**2l**): Colorless oil. IR (KBr) cm^{-1}: 1680 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.84 (3H, s, OCH_3), 4.25 (2H, s, CH_2), 6.75—7.75 (9H, m, aromatic H). 2,4-Dinitrophenylhydrazone: Orange scales (MeOH), 163—164 °C. *Anal.* Calcd for $C_{21}H_{18}N_4O_5$: C, 62.06; H, 4.46; N, 13.79. Found: C, 62.00; H, 4.44; N, 13.90.

Reaction of 3,4-Dimethyl-2-(α-benzyloxybenzyl)thiazolium Iodide (5a) with Cs_2CO_3 A mixture of 3,4-dimethyl-2-(α-benzyloxybenzyl)thiazolium iodide (**5a**, 1310 mg, 3 mmol) and Cs_2CO_3 (1750 mg, 3.3 mmol) in THF (30 ml) was refluxed for 3 h with stirring. The reaction mixture was poured into ice-H_2O and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with hexane and AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave deoxybenzoin (**2a**) in 4% (26 mg) yield. Further purification was difficult.

Reaction of 1-Methyl-2-(α-benzyloxybenzyl)pyridinium Iodide (6a) with Cs_2CO_3 A mixture of 1-methyl-2-(α-benzyloxybenzyl)pyridinium iodide (**6a**, 1250 mg, 3 mmol) and Cs_2CO_3 (1075 mg,) in THF (30 ml) was refluxed for 4 h with stirring. The reaction mixture was poured into

ice-H_2O and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane and AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave a mixture (240 mg), and the formation of deoxybenzoin (**2a**) was detected by HPLC and ^{1}H-NMR spectroscopy. However, purification was difficult.

Reaction of 1-Methyl-2-(α-benzyloxybenzyl)-1*H*-benzimidazole (7a) with Base A solution of 1-methyl-2-(α-benzyloxybenzyl)benzimidazole (**7a**, 621 mg, 1.89 mmol) and NaH (60% in oil, 120 mg, 3 mmol) in 10 ml of DMF was stirred at 50 °C for 1 h. The reaction mixture was poured into ice-H_2O, and the separated solid was collected, washed with H_2O, and dried. The solid was recrystallized from benzene to give 1-methyl-2-(α-hydroxy-α-benzylbenzyl)imidazole (**10a**, 440 mg, 71%), colorless needles, mp 136—139 °C. IR (KBr) cm^{-1}: 3380 (OH). ^{1}H-NMR (DMSO-d_6) δ: 3.44 (3H, s, N–Me), 3.80 (2H, b, CH_2), 6.40 (1H, s, OH), 6.82—7.88 (14H, m, aromatic H). EI-MS: Calcd for $C_{22}H_{20}N_2O$: 328.15756. Observed: 328.15751. In the case of the reaction with K_2CO_3, work-up as described above recovered the starting **7a**.

Reaction of 1-Methyl-2-(α-benzyloxybenzyl)-1*H*-imidazole (8a) with NaH Sodium hydride (NaH, 60% in oil, 163 mg, 4.08 mmol) was added to a solution of 1-methyl-2-(α-benzyloxybenzyl)-1*H*-imidazole (**8a**, 758 mg, 2.72 mmol) in 10 ml of DMF, and the mixture was stirred at 50 °C for 1 h. The reaction mixture was poured into ice-H_2O, and extracted with AcOEt. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The starting **8a** was recovered quantitatively.

Reaction of 4-Methyl-2-(α-benzyloxybenzyl)thiazole (9a) with NaH A solution of 4-methyl-2-(α-benzyloxybenzyl)thiazole (**9a**, 385 mg, 1.3 mmol) and NaH (60% in oil, 78 mg, 1.95 mmol) in 4 ml of DMF was stirred at 50 °C for 1 h. The reaction mixture was poured into ice-H_2O and extracted with AcOEt. The organic layer was washed with H_2O and dried over Na_2SO_4. The solvent was evaporated and residual solid was washed with hexane to give 4-methyl-2-(α-hydroxy-α-benzylbenzyl)thiazole (**11a**, 149 mg, 38%), colorless needles (*n*-hexane), mp 103—105 °C. *Anal.* Calcd for $C_{18}H_{18}NOS$: C, 76.10; H, 5.17; N, 4.23. Found: C, 75.84; H, 5.09; N, 4.17. IR (KBr) cm^{-1}: 3330 (OH). ^{1}H-NMR ($CDCl_3$) δ: 3.52 (1H, d, J = 12 Hz, CH_2), 4.10 (1H, d, J = 12 Hz, CH_2), 7.06—8.11 (14H, m, aromatic H).

Cross Reaction between 1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodide (1a) and 1,3-Dimethyl-2-[α-(4-methylbenzyloxy)-4-methylbenzyl]benzimidazolium Iodide (1e) with Cs_2CO_3 Cesium carbonate (Cs_2CO_3, 2350 mg, 7.24 mmol) was added to a mixture of benzimidazolium salts **1a** (1410 mg, 3 mmol) and **1e** (1490 mg, 3 mmol) in 60 ml of THF, and the mixture was refluxed for 16 h. The reaction mixture was poured into ice-H_2O, and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was passed through a column of SiO_2 with *n*-hexane–AcOEt (20 : 1). The first fraction gave the mixture of deoxybenzoins **2a**, **2c**, **2e** and **2f**. The ratio of the deoxybenzoins was determined from the ^{1}H-NMR spectrum based on integration of methylene proton signals of the deoxybenzoins **2**. Chemical shifts (δ) of the deoxybenzoins: **2a**, 4.29 ppm; **2c**, 4.24 ppm; **2e**, 4.21 ppm; and **2f**, 4.26 ppm.

Cross Reaction between 1,3-Dimethyl-2-[α-(4-methylbenzyloxy)benzyl]-benzimidazolium Iodide (1c) and 1,3-Dimethyl-2-(α-benzyloxy-4-methylbenzyl)benzimidazolium Iodide (1f) with Cs_2CO_3 Cesium carbonate (Cs_2CO_3, 2350 mg, 7.24 mmol) was added to a mixture of benzimidazolium salts **1c** (1450 mg, 3 mmol) and **1f** (1450 mg, 3 mmol) in 60 ml of THF, and the mixture was refluxed for 16 h with stirring. The reaction mixture was poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt (20 : 1). The first fraction gave the mixture of deoxybenzoins (**2a**, **2c**, **2e**, and **2f**). The ratio was determined from the ^{1}H-NMR spectrum based on integration of the methylene proton signals of the deoxybenzoins **2**.

Reaction of 2-Benzoyl-1,3-dimethylbenzimidazolium Iodide (14) with Benzylmagnesium Chloride (13) A solution of benzylmagnesium chloride (**13**, prepared from 127 μl of benzyl chloride and 72 mg of Mg in 5 ml of THF) was added to a solution of 2-benzoyl-1,3-dimethylbenzimidazolium iodide (**14**,[13] 378 mg, 1 mmol) in 5 ml of THF, and the mixture was refluxed for 1 h with stirring. The reaction mixture was poured into NH_4Cl–NH_3–H_2O solution and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane and AcOEt. The fraction eluted with AcOEt gave a mixture of **2a** and **15** (110 mg). The structures were determined by comparison with authentic samples based on the retention times in HPLC and chemical shifts of the methylene protons in ^{1}H-NMR (**2a** : **15** = 8 : 13).

Cross Reaction between 1,3-Dimethyl-2-(α-benzyloxy-4-methylbenzyl)-benzimidazolium Iodide (1f) and 2-Benzoyl-1,3-dimethylbenzimidazolium Iodide (14) with Cs_2CO_3 A mixture of azolium salts **1f** (484 mg, 1 mmol) and **14**[13] (378 mg, 1 mmol), and Cs_2CO_3 (325 mg, 1 mmol) in THF (30 ml) was refluxed for 16 h with stirring. The reaction mixture was poured into ice-H_2O mixture, and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt (20 : 1). The first fraction eluted with *n*-hexane–AcOEt (20 : 1) gave a mixture of deoxybenzoins **2a** and **2f**. The ratio was determined from the ^{1}H-NMR spectrum based on integration of the methylene proton signals of the deoxybenzoins.

Reaction of 1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodide (1a) with K_2CO_3 in MeOH A mixture of azolium salt (**1a**, 1410 mg, 3 mmol) and K_2CO_3 (450 mg, 3.26 mmol) in MeOH (15 ml) was refluxed for 4 h with stirring. The reaction mixture was poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was passed through a column of SiO_2 with n-hexane and AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave methyl benzoate (**12**) in 74% (301 mg) yield.

1-Methyl-2-(α-benzyloxybenzyl)benzimidazoles 17 General Procedure: Sodium hydride (NaH, 60% in oil, 1900 mg, 47.5 mmol) was added to a solution of 1-methyl-2-(α-hydroxybenzyl)benzimidazole[11] (**16**, 40 mmol) and benzyl bromide (50 mmol) in 150 ml of DMF, and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt then CH_2Cl_2. The fraction eluted with CH_2Cl_2 gave **17**. The yields and spectral data for the products synthesized are shown in Tables 3 and 4.

1,3-Dimethyl-2-(α-benzyloxybenzyl)benzimidazolium Iodide 1 General Procedure: A solution of 1-methyl-2-(α-benzyloxybenzyl)benzimidazole (**17**, 41 mmol) and methyl iodide (10 ml) in 10 ml of DMF was heated at 70 °C for 1 h with stirring. Diethyl ether (Et_2O, 50 ml) was added to the reaction mixture. The separated solid was collected, washed with ether, and dried. The solid was recrystallized with acetone to give the quaternary salt **1**. The yields and spectral data for the products synthesized are shown in Tables 1 and 2.

1-Methyl-2-(α-benzyloxybenzyl)imidazole 19 General Procedure: Sodium hydride (NaH, 60% in oil, 820 mg, 20.5 mmol) was added to a solution of 1-methyl-2-(α-hydroxybenzyl)imidazole[11] (**18**, 20 mmol) and benzyl bromide (2.5 ml, 21 mmol) in 150 ml of DMF, and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane and AcOEt then CH_2Cl_2. The fraction eluted with CH_2Cl_2 gave **19**. The yields and spectral data for the products synthesized are shown in Tables 3 and 4.

1,3-Dimethyl-2-(α-benzyloxybenzyl)imidazolium Iodide 4 General Procedure: A solution of 1-methyl-2-(α-benzyloxybenzyl)imidazole (**19**, 484 mg, 1.7 mmol) and methyl iodide (1 ml) in 1 ml of acetonitrile was refluxed for 1 h with stirring. The mixture was concentrated under reduced pressure. The residue was washed with ether and dried to give **4**. The yields and spectral data for the products synthesized are shown in Tables 1 and 2.

2-(α-Benzyloxybenzyl)-4-methylthiazole (21) Sodium hydride (NaH, 60% in oil, 840 mg, 21 mmol) was added to a stirred solution of 2-(α-hydroxybenzyl)-4-methylthiazole (**20**, 4100 mg, 20 mmol) in 50 ml of THF, and the mixture was further stirred for 15 min at room temperature. A solution of benzyl bromide (2.5 ml, 21 mmol) was slowly added to the cooling mixture below 5 °C. The mixture was stirred for 1 h at 5 °C and for 16 h at room temperature, then poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt (20 : 1). The first fraction gave **21** in 94% (5540 mg) yield. Colorless oil. Formula: $C_{18}H_{17}NOS$ (M.W. = 295.40). FAB-MS *m/z*: 296 [$(M+H)^+$]. ^{1}H-NMR ($CDCl_3$) δ:

Table 1. Yields, Formula, and Elemental Analyses for the Azolium Salts **1** and **4**

Compd.	Yield (%)	Appearance	mp (°C)	Formula	Elementary analysis (%) Calcd (Found)			FAB-MS (*m/z*)
					C	H	N	
1a	90	Colorless needles (acetone)	172—175	$C_{23}H_{23}IN_2O$	58.73 (58.27	4.93 4.95	5.95 5.66)	343 [$(M-I)^+$]
1b	89	Colorless needles (acetone)	150—152	$C_{23}H_{22}ClIN_2O$	54.72 (54.22	4.37 4.39	5.55 5.62)	377 [$(M-I)^+$]
1c	84	Colorless needles (acetone)	151—153	$C_{24}H_{25}IN_2O$	59.51 (59.48	5.20 5.32	5.78 5.76)	357 [$(M-I)^+$]
1d	90	Colorless needles (acetone)	187—189	$C_{24}H_{25}IN_2O_2$	57.60 (57.42	5.04 4.82	5.60 5.34)	373 [$(M-I)^+$]
1e	83	Colorless needles (acetone)	193—196	$C_{25}H_{27}IN_2O$	60.24 (60.27	5.46 5.57	5.62 5.50)	371 [$(M-I)^+$]
1f	94	Colorless needles (acetone)	214—216	$C_{24}H_{25}IN_2O$	59.51 (59.43	5.20 5.22	5.75 5.63)	357 [$(M-I)^+$]
1g	75	Colorless needles (acetone)	144—146	$C_{24}H_{25}IN_2O_2$	57.61 (57.22	5.04 4.94	5.60 5.37)	
4a	99	Colorless oil		$C_{19}H_{21}IN_2O$				293 [$(M-I)^+$]
4b	99	Colorless oil		$C_{19}H_{20}ClIN_2O$				327 [$(M-I)^+$]
4c	97	Colorless oil		$C_{20}H_{23}IN_2O_2$				323 [$(M-I)^+$]
4g	99	Colorless oil		$C_{20}H_{23}IN_2O_2$				323 [$(M-I)^+$]
4h	89	Colorless oil		$C_{20}H_{22}ClIN_2O_2$				357 [$(M-I)^+$]
4i	91	Colorless oil		$C_{21}H_{25}IN_2O_2$				337 [$(M-I)^+$]
4j	99	Colorless oil		$C_{21}H_{25}IN_2O_3$				353 [$(M-I)^+$]
4k	99	Colorless oil		$C_{20}H_{23}IN_2O_2$				323 [$(M-I)^+$]
4l	96	Colorless prisms (acetone)	162—162.5	$C_{20}H_{23}IN_2O_2$	53.34 (53.70	5.15 5.24	6.22 6.07)	

Table 2. ^{1}H-NMR Spectral Data for the Azolium Salts **1** and **4**

Compd.	^{1}H-NMR (DMSO-d_6) δ (ppm) and J (Hz)
1a	4.09 (6H, s, 2×NMe), 4.89 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.93 (1H, d, J=11, CH$_a\underline{H}_b$), 6.84 (1H, s, CH), 7.18—7.56 (10H, m, aromatic H), 7.60—8.13 (4H, m, aromatic H)
1b	4.09 (6H, s, 2×NMe), 4.88 (2H, s, CH_2), 6.83 (1H, s, CH), 7.38—7.49 (9H, m, aromatic H), 7.58—8.15 (4H, m, aromatic H)
1c	2.14 (3H, s, Me), 4.05 (6H, s, 2×NMe), 4.80 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.86 (1H, d, J=11, CH$_a\underline{H}_b$), 6.77 (1H, s, CH), 7.00 (2H, d, J=9, aromatic H), 7.30 (2H, d, J=9, aromatic H), 7.42 (5H, s, aromatic H), 7.56—8.11 (4H, m, aromatic H)
1d	3.62 (3H, s, OMe), 4.07 (6H, s, 2×NMe), 4.82 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.87 (1H, d, J=11, CH$_a\underline{H}_b$), 6.77 (1H, s, CH), 6.76 (2H, d, J=9, aromatic H), 7.34 (2H, d, J=9, aromatic H), 7.42 (5H, s, aromatic H), 7.57—8.12 (4H, m, aromatic H)
1e	2.17 (3H, s, Me), 2.32 (3H, s, Me), 4.05 (6H, s, 2×NMe), 4.80 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.84 (1H, d, J=11, CH$_a\underline{H}_b$), 6.69 (1H, s, CH), 6.88—7.48 (8H, m, aromatic H), 7.48—8.18 (4H, m, aromatic H)
1f	2.33 (3H, s, Me), 4.09 (6H, s, 2×NMe), 4.88 (2H, s, CH_2), 6.77 (1H, s, CH), 7.09—7.53 (9H, m, aromatic H), 7.58—8.64 (4H, m, aromatic H)
1g	3.75 (3H, s, OMe), 4.07 (6H, s, 2×NMe), 4.83 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.89 (1H, d, J=11, CH$_a\underline{H}_b$), 6.74 (1H, s, CH), 6.78—8.18 (13H, m, aromatic H)
4a	3.78 (6H, s, 2×NMe), 4.73 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.79 (1H, d, J=11, CH$_a\underline{H}_b$), 6.46 (1H, s, CH), 7.21—7.48 (10H, m, aromatic H), 7.71 (2H, s, imidazole ring H)
4b	3.82 (6H, s, 2×NMe), 4.72 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.78 (1H, d, J=11, CH$_a\underline{H}_b$), 6.48 (1H, s, CH), 7.22—7.48 (9H, m, aromatic H), 7.74 (2H, s, imidazole ring H)
4c	3.70 (3H, s, OMe), 3.75 (6H, s, 2×NMe), 4.62 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.67 (1H, d, J=11, CH$_a\underline{H}_b$), 6.35 (1H, s, CH), 6.75 (2H, d, J=9, aromatic H), 7.24 (2H, d, J=9, aromatic H), 7.28 (5H, m, aromatic H), 7.63 (2H, s, imidazole ring H)
4g	3.78 (3H, s, OMe), 3.81 (6H, s, 2×NMe), 4.75 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.81 (1H, d, J=11, CH$_a\underline{H}_b$), 6.45 (1H, s, CH), 6.71—7.44 (9H, m, aromatic H), 7.67 (2H, s, imidazole ring H)
4h	3.75 (3H, s, OMe), 3.80 (6H, s, 2×NMe), 4.71 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.76 (1H, d, J=11, CH$_a\underline{H}_b$), 6.41 (1H, s, CH), 6.69—7.39 (8H, m, aromatic H), 7.70 (2H, s, imidazole ring H)
4i	2.30 (3H, s, Me), 3.77 (3H, s, OMe), 3.78 (6H, s, 2×NMe), 4.67 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.72 (1H, d, J=11, CH$_a\underline{H}_b$), 6.38 (1H, s, CH), 6.68—7.41, (8H, m, aromatic H), 7.69 (2H, s, imidazole ring H)
4j	3.74 (6H, s, 2×OMe), 3.77 (6H, s, 2×NMe), 4.64 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.68 (1H, d, J=11, CH$_a\underline{H}_b$), 6.35 (1H, s, CH), 6.65—7.41 (8H, m, aromatic H), 7.67 (2H, s, imidazole ring H)
4k	3.74 (3H, s, OMe), 3.88 (6H, s, 2×NMe), 4.79 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.83 (1H, d, J=11, CH$_a\underline{H}_b$), 6.52 (1H, s, CH), 6.93 (2H, d, J=9, aromatic H), 7.31 (2H, d, J=9, aromatic H), 7.33 (5H, m, aromatic H), 7.77 (2H, s, imidazole ring H)
4l	3.72 (3H, s, OMe), 3.77 (6H, s, 2×NMe), 4.69 (1H, d, J=11, C$\underline{H}_a$H$_b$), 4.78 (1H, d, J=11, CH$_a\underline{H}_b$), 6.33 (1H, s, CH), 6.92—7.48 (9H, m, aromatic H), 7.66 (2H, s, imidazole ring H)

Table 3. Yields, Formula, and Elemental Analyses for the Azoles **17** and **19**

Compd.	Yield (%)	Appearance	mp (°C)	Formula	Elementary analysis (%) Calcd (Found)			FAB-MS (*m/z*)
					C	H	N	
17a	99	Colorless oil		$C_{22}H_{20}N_2O$				329 [(M+H)$^+$]
17b	86	Colorless oil		$C_{22}H_{19}ClN_2O$				363 [(M+H)$^+$]
17c	87	Colorless oil		$C_{23}H_{22}N_2O$				343 [(M+H)$^+$]
17d	78	Colorless oil		$C_{23}H_{22}N_2O_2$				359 [(M+H)$^+$]
17e	96	Colorless oil		$C_{24}H_{24}N_2O$				357 [(M+H)$^+$]
17f	99	Colorless oil		$C_{23}H_{22}N_2O$				343 [(M+H)$^+$]
17g	98	Colorless columns (*n*-hexane)	75—76	$C_{23}H_{22}N_2O_2$	77.07 (77.29	6.19 6.34	7.82 7.85)	
19a	99	Colorless oil		$C_{18}H_{18}N_2O$				279 [(M+H)$^+$]
19b	99	Colorless prisms (*n*-hexane)	66—67	$C_{18}H_{17}ClN_2O$	69.12 (69.22	5.48 5.39	8.95 9.03)	313 [(M+H)$^+$]
19c	59	Colorless oil		$C_{19}H_{20}N_2O$				293 [(M+H)$^+$]
19g	87	Colorless oil		$C_{19}H_{20}N_2O_2$				309 [(M+H)$^+$]
19h	86	Colorless oil		$C_{19}H_{19}ClN_2O_2$				343 [(M+H)$^+$]
19i	93	Colorless oil		$C_{20}H_{22}N_2O_2$				323 [(M+H)$^+$]
19j	74	Colorless oil		$C_{20}H_{22}N_2O_3$				339 [(M+H)$^+$]
19k	99	Colorless oil		$C_{19}H_{20}N_2O_2$				309 [(M+H)$^+$]
19l	83	Colorless oil		$C_{19}H_{20}N_2O_2$				309 [(M+H)$^+$]

Table 4. ^{1}H-NMR Spectral Data for the Azoles **17** and **19**

Compd.	^{1}H-NMR ($CDCl_3$) δ (ppm) and J (Hz)
17a	3.56 (3H, s, NMe), 4.66 (2H, s, CH_2), 6.06 (1H, s, CH), 7.15 (13H, m, aromatic H), 7.75—7.97 (1H, m, aromatic H)
17b	3.52 (3H, s, NMe), 4.61 (2H, s, CH_2), 6.00 (1H, s, CH), 7.19—7.50 (12H, m, aromatic H), 7.69—7.85 (1H, m, aromatic H)
17c	2.33 (3H, s, Me), 3.55 (3H, s, NMe), 4.61 (2H, s, CH_2), 6.01 (1H, s, CH), 6.90—7.50 (12H, m, aromatic H), 7.69—7.95 (1H, m, aromatic H)
17d	3.54 (3H, s, NMe), 3.76 (3H, s, OMe), 4.56 (2H, s, CH_2), 5.99 (1H, s, CH), 6.83 (2H, d, J=9, aromatic H), 7.13—7.55 (10H, m, aromatic H), 7.68—7.89 (1H, m, aromatic H)
17e	2.31 (6H, s, 2×Me), 3.56 (3H, s, NMe), 4.59 (2H, s, CH_2), 5.99 (1H, s, CH), 6.96—7.46 (11H, m, aromatic H), 7.64—7.95 (1H, m, aromatic H)
17f	2.35 (3H, s, Me), 3.58 (3H, s, NMe), 4.67 (2H, s, CH_2), 6.03 (1H, s, CH), 7.09—7.53 (12H, m, aromatic H), 7.69—7.96 (1H, m, aromatic H)
17g	3.67 (3H, s, OMe), 3.69 (3H, s, NMe), 4.58 (2H, s, CH_2), 5.97 (1H, s, CH), 6.75—7.75 (13H, m, aromatic H)
19a	3.34 (3H, s, NMe), 4.54 (2H, s, CH_2), 5.79 (1H, s, CH), 6.74 (1H, br s, imidazole ring H), 6.95 (1H, br s, imidazole ring H), 7.13—7.53 (10H. m, aromatic H)
19b	3.34 (3H, s, NMe), 4.50 (2H, s, CH_2), 5.77 (1H, s, CH), 6.76 (1H, br s, imidazole ring H), 6.96 (1H, br s, imidazole ring H), 7.14—7.49 (9H, m, aromatic H)
19c	3.36 (3H, s, NMe), 3.76 (3H, s, OMe), 4.46 (2H, s, CH_2), 5.76 (1H, s, CH), 6.76 (1H, br s, imidazole ring H), 6.89 (2H, d, J=9, aromatic H), 6.89 (1H, br s, imidazole ring H), 7.12 (2H, d, J=9, aromatic H), 7.27 (5H, m, aromatic H)
19g	3.39 (3H, s, NMe), 3.72 (3H, s, OMe), 4.53 (2H, s, CH_2), 5.77 (1H, s, CH), 6.68—7.45 (11H, m, aromatic H)
19h	3.37 (3H, s, NMe), 3.73 (3H, s, OMe), 4.51 (2H, s, CH_2), 5.75 (1H, s, CH), 6.76 (1H, br s, imidazole ring H), 6.95 (1H, b, imidazole ring H), 6.72—7.52 (9H, m, aromatic H)
19i	2.31 (3H, s, Me), 3.37 (3H, s, NMe), 3.72 (3H, s, OMe), 4.49 (2H, s, CH_2), 5.75 (1H, s, CH), 6.61—7.36, (10H, m, aromatic H)
19j	3.40 (3H, s, NMe), 3.75 (3H, s, OMe), 3.78 (3H, s, OMe), 4.49 (2H, s, CH_2), 5.77 (1H, s, CH), 6.76 (1H, br s, imidazole ring H), 6.96 (1H, br s, imidazole ring H), 6.72—7.45 (8H, m, aromatic H)
19k	3.48 (3H, s, NMe), 3.74 (3H, s, OMe), 4.52 (2H, s, CH_2), 5.72 (1H, s, CH), 6.76 (1H, br s, imidazole ring H), 6.89 (2H, d, J=9, aromatic H), 6.95 (1H, br s, imidazole ring H), 7.25 (2H, d, J=9, aromatic H), 7.30 (5H, m, aromatic H)
19l	3.44 (3H, s, NMe), 3.65 (3H, s, OMe), 4.50 (2H, s, CH_2), 5.99 (1H, s, CH), 6.69 (1H, br s, imidazole ring H), 6.90 (1H, br s, imidazole ring H), 6.76—7.90 (9H, m, aromatic H)

2.36 (3H, s, CH_3), 4.59 (2H, s, CH_2), 5.70 (1H, s, CH), 6.77 (1H, s, thiazole ring H), 7.10—7.51 (10H, m, aromatic H).

3,4-Dimethyl-2-(α-benzyloxybenzyl)thiazolium Iodide (5a) A mixture of 2-(α-benzyloxybenzyl)-4-methylthiazole (**21**, 5.00 g, 17 mmol) and methyl iodide (10 ml) in DMF (6 ml) was heated at 80 °C for 16 h. After cooling to room temperature, the mixture was added to Et_2O. The separated solid was collected and dried. The thiazolium salt **5a** was obtained in 88% (6540 mg) yield. Formula: $C_{19}H_{20}INOS$ (M.W.= 437.33). FAB-MS *m/z*: 310 [(M−I)$^+$]. ^{1}H-NMR (DMSO-d_6) δ: 2.50 (3H, s, CH_3), 3.69 (3H, s, NCH_3), 4.66 (2H, s, CH_2), 6.27 (1H, s, CH), 7.30 (5H, s, aromatic H), 7.48 (5H, m, aromatic H), 7.84 (1H, s, thiazole ring H).

2-(α-Hydroxybenzyl)pyridine (23) Sodium borohydride ($NaBH_4$, 524 mg, 14 mmol) was added to a solution of 2-benzoylpyridine (**22**, 9.15 g, 50 mmol) in 100 ml of MeOH, and the resulting mixture was stirred at room temperature for 1 h. Acetone (2 ml) was added to the solution, and the mixture was stirred for 0.5 h, poured into ice-H_2O mixture, and extracted with benzene. The organic layer was washed with H_2O, dried over Na_2SO_4, and concentrated. The obtained residue was washed with *n*-hexane to give **23** in 97% (8.96 g) yield. Colorless needles (acetone–*n*-hexane). IR (KBr) cm^{-1}: 3100 (OH). ^{1}H-NMR ($CDCl_3$) δ: 5.25 (1H, br s), 5.72 (1H, s), 7.00—7.75 (8H, m, aromatic H), 8.50 (1H, d, J=5 Hz, aromatic H).

2-(α-Benzyloxybenzyl)pyridine (24) Benzyl bromide (2.5 ml) was added to a solution of **23** (3.75 g, 20 mmol) and NaH (60% in oil, 820 mg, 20.5 mmol) in 50 ml of DMF, and the mixture was stirred at room temperature for 16 h, then poured into ice-H_2O mixture and extracted with benzene. The organic layer was washed with H_2O, dried over

Na_2SO_4, and concentrated. The residue was purified by column chromatography on SiO_2 with *n*-hexane–AcOEt. The fraction eluted with *n*-hexane–AcOEt (20 : 1) gave **24** in 99% (5.5 g) yield. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 4.55 (2H, s, CH_2), 5.56 (1H, s), 7.00—7.85 (13H, m), 8.50 (1H, d, J=5 Hz). FAB-MS *m/z*: 276 [$(M+H)^+$].

1-Methyl-2-(α-benzyloxybenzyl)pyridinium Iodide (6a) A mixture of **24** (284 mg, 1.02 mmol) and methyl iodide (0.5 ml) in acetonitrile (2 ml) was refluxed for 4 h with stirring, then cooled to room temperature, and Et_2O was added to it. The resulting mixture was allowed to stand at room temperature overnight and the separated solid was collected. The solid was washed with a small portion of acetonitrile and dried to give **6a**. Yellowish powder. ^{1}H-NMR (DMSO-d_6) δ: 4.30 (3H, s, Me), 4.70 (2H, s, CH_2), 7.49 (5H, s, Ph), 7.50 (5H, s, Ph), 7.98—8.40 (2H, m, pyridine ring H), 8.50—8.77 (1H, m, pyridine ring H), 9.11 (1H, d, J=5 Hz, pyridine ring H). FAB-MS *m/z*: 290 [$(M-I)^+$].

References and Notes

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13) 2-Benzoyl-1,3-dimethylbenzimidazolium iodide (**14**) was prepared from 1-methylbenzimidazole through lithiation, addition of benzonitrile, hydrolysis, and quaternization. The details will be reported elsewhere.