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Ring-methylation of pyrrole and indole using supercritical methanol

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ABSTRACT

The ring-methylation of pyrrole or indole using supercritical methanol proceeded at 623 K without the further addition of catalysts. Pyrrole produced a mixture of unreacted pyrrole and mono-, di-, tri-, and tetra-methylpyrroles at the reaction time of 8 h. On the other hand, indole was selectively methylated at the C3 position to afford 3-methylindole in 79% yield at the reaction time of 5 h. The ring-methylation of indole using supercritical methanol was claimed to proceed via (1*H*-indol-3-yl)methanol. The conversion of indole to (1*H*-indol-3-yl)methanol would be achieved by the electrophilic aromatic substitution between the indol-1-ide (indole anion) and H_2C^+—OH. The (1*H*-indol-3-yl)methanol must be reduced to 3-methylindole in the presence of supercritical methanol.

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1. Introduction

The transformation of organic compounds using supercritical fluids as the reaction media and reagents has attracted much attention in the field of organic syntheses.[1,2] For example, supercritical methanol (T_c=513 K, p_c=8.1 MPa, d_c=0.273 kg dm^{-3}) methylates the hydroquinone ring without adding additional catalysts to afford 2-methylbenzene-1,4-diol as the major product.[3,4] Thus far aromatic compounds containing no phenolic OH group have not methylated using supercritical methanol. These findings indicate that the phenolic OH group plays an important role in the ring-methylation. Takebayashi et al. investigated the non-catalytic *o*-methylation of phenol in supercritical methanol and found that the supercritical *o*-methylation was retarded by acid and accelerated by base.[5] Taking into account the acid/base effect and *o*-selectivity, they proposed that the phenolic OH group acts as an acid catalyst for the supercritical methylation of its own molecule. Pyrroles and indoles containing NH groups are known to be as acidic as typical alcohols. Thus, it is reasonable to assume that pyrrole and indole rings could be methylated using supercritical methanol without the further addition of catalysts. Furthermore, it is well known that supercritical methanol can be employed as an *N*-methylating reagent for amines.[3,6–8] Thus, it is interesting which atom, the C or the N of the nitrogen heterocycles, is methylated. In this article, we report the results of the ring-methylation of pyrrole and indole using supercritical methanol. Moreover, we propose a reaction mechanism for the ring-methylation of indole.

2. Results and discussion

2.1. Methylation of pyrrole using supercritical methanol

A 0.140×10^{-4} dm^3 portion of a methanol solution of pyrrole, 1-methylpyrrole, furan or pyridine (0.10 mol dm^{-3}) was subjected to reactions at 623 K in a sealed Pyrex reactor. The calculated densities of the methanol in the reactor are around 0.29 kg dm^{-3} at the critical temperature or above (≥513 K). The densities are beyond the critical one for methanol (0.273 kg dm^{-3}). The reactions were carried out without the further addition of any catalysts. After the reaction for 8 h, the reaction mixture was analyzed using the GC (DB-17) and GC–MS (DB-5MS). Table 1 shows the results of the GC–MS and GC analyses of the reaction mixture.

The prominent peaks of $M^{+\bullet}$ (the molecular ion) indicate that pyrrole is methylated at 623 K in the presence of supercritical methanol to afford a mixture of unreacted pyrrole and mono-, di-, tri-, and tetra-methylpyrroles. It appears that the pyrrole ring is

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Table 1
GC–MS and GC analyses of the reaction mixture from the methanol solution of pyrrole

MS m/z $M^{+\cdot}$	Change in molecular weight ($M^{+\cdot}-67$)[a]	Number of CH_3 group	Ratio of GC area (retention time/min)[b]
67	0	0	1.0 (6.7)
81	14	1	1.5 (9.1)
95	28	2	4.5 (11.1)
109	42	3	4.7 (12.9)
123	56	4	2.2 (14.9)

Reaction conditions: Initial concentration of pyrrole=0.10 mol dm^{-3}, reaction temperature=623 K, reaction time=8 h.
[a] The value of ($M^{+\cdot}-67$) is the molecular-weight difference between the product (molecular weight=M) and pyrrole (molecular weight=67).
[b] Temperature program of the GC (DB-17 30-m column, FID); 313 K for 5 min→10 K rise/min to 523 K.

easily methylated at 623 K using supercritical methanol, and it is difficult to stop the reaction after a single methylation. The formation of the poly-methyl pyrroles appears to be unavoidable. The supercritical methylation of pyrrole appears to have important limitations as a procedure for the selective preparation of the mono-, di-, tri-, or tetra-methylpyrrole, whereas it was reported that the supercritical methylation of phenol would be a promising way for preparing *o*-cresol.[5] The smooth formation of poly-methyl pyrroles suggests that the active methylating species is an electrophile, because pyrrole is a π-sufficient heterocycle.

The results of the GC analyses of the reaction mixtures from the methanol solutions of 1-methylpyrrole, furan, and pyridine showed no peaks other than the substrates and the solvent (data not shown). These findings suggest that the pyrrol-1-ide (pyrrole anion) generated from the pyrrole plays an important role in the supercritical methylation of the pyrrole ring as the phenoxide generated from phenol has an important role in the supercritical *o*-methylation of the phenol ring.[5]

2.2. Methylation of indole using supercritical methanol

Indole contains a pyrrole ring with a benzene ring fused to the side. Gopal et al. reported the methylation of indole using vapor-phase methanol over zeolites.[9] Methylation mainly occurs at the C3 position of the indole. The maximum 3-methylindole yield of 33.6% at the 72.6% indole-conversion was attained over a 3 wt % CeHY catalyst at 573 K. Under the best conditions with respect to the yield of 3-methylindole, the selectivity for 3-methylindole was less than 50%, and the major by-products were 2,3-dimethylindole and polymethyl-indolenines, such as 3,3-dimethylindolenine, 2,3,3-trimethylindolenine, and 1,2,3,3-tetramethylindolenine. This indicates that the poly-methylation of indole reduced the selectivity for 3-methylindole. In order to improve the selectivity and the yield of 3-methylindole, we attempted the methylation of indole at 623 K without the addition of the zeolite-catalyst, which would accelerate the poly-methylation. In our investigation, supercritical methanol was employed instead of the vapor-phase one.

The ^{1}H NMR spectrum of the reaction mixture at the reaction time of 1 h was measured after removal of the solvent in vacuo. Figure 1 shows the ^{1}H NMR spectra (6.0–8.0 ppm, $CDCl_3$, TMS) of the authentic 2- and 3-methylindoles, and the reaction mixture.

In the ^{1}H NMR spectrum of the reaction mixture there are peaks at around 6.9–7.0 ppm (*H*–C2) and at around 7.8–7.9 ppm (*H*–N), but there is no peak at around 6.2 ppm, which is the *H*–C3 signal of 2-methylindole. This finding indicates that the methylation of indole using supercritical methanol preferentially gives rise to 3-methylindole. The small peak at around 6.5–6.6 ppm in the spectrum of the reaction mixture will be due to the *H*–C3 of the unreacted indole. It is well known that electrophilic aromatic

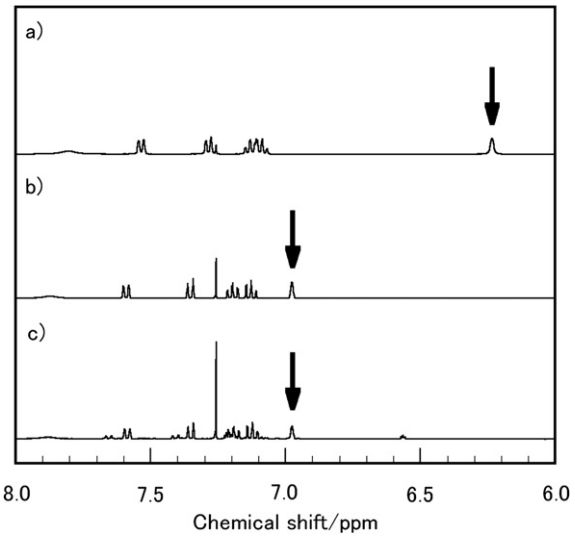


Figure 1. ^{1}H NMR spectra of authentic 2- and 3-methylindoles, and the reaction mixture: (a) 2-methylindole, (b) 3-methylindole, and (c) the reaction mixture. Initial concentration of indole=0.10 mol dm^{-3}. Reaction temperature=623 K. Reaction time=1 h.

substitution on indole is preferred at the C3 with almost all electrophiles, because the C3 is the most electron-rich, most nucleophilic position on the ring. Thus, the preferential formation of 3-methylindole during the supercritical methylation suggests that the methylating species in supercritical methanol attacks at the C3 position of the indole as an electrophile.

Figure 2 shows the time courses of the reactions of indole in the presence of supercritical methanol, when a 1.20×10^{-4} dm^3 portion of the 0.10 mol dm^{-3} methanol solution of indole was subjected to reactions at 623 K.

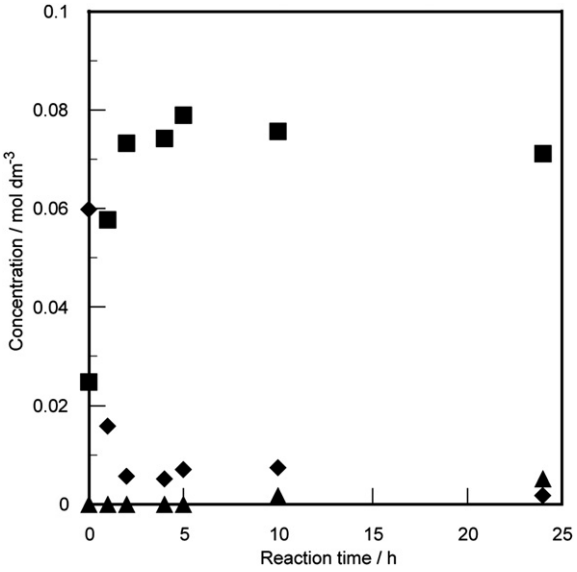


Figure 2. Time courses of the reactions of indole in the presence of supercritical methanol: (◆) indole; (■) 3-methylindole; (▲) 2,3-dimethylindole. Initial concentration of indole=0.10 mol dm^{-3}. Reaction temperature=623 K.

The concentration of 3-methylindole reaches the maximum value at the reaction time of 4–5 h, and thereafter gradually decreases. The concentration of 2,3-dimethylindole is negligible for the first 10 h, and then gradually increases with an increase in the reaction time. It appears that the conversion of 3-methylindole to 2,3-dimethylindole is difficult when compared to the single-methylation of indole. The

methylation of 3-methylindole to 2,3-dimethylindole may proceed via the 3,3-dimethyl-3*H*-indolium.[10]

In addition, it is not possible that an electrophile attacks an indole molecule at the C2 without seriously disturbing the aromaticity of the fused benzene ring. The loss of the aromaticity of the intermediate giving 2-methylindole would be a reason why indole afforded much less poly-methylated products than pyrrole did.

Table 2 shows the conversion of indole, the attained yield and the selectivity of 3-methylindol using supercritical methanol at 623 K for 4 h, together with the reported values using the vapor-phase methanol at 573 K for 1 h over the CeHY catalyst.[9] As can be seen in the table, the conversion, the yield, and the selectivity of the supercritical methylation were much higher than those attained using vapor-phase methanol over the CeHY catalyst. It can be assumed that no added catalyst depresses the poly-methylation of indole. Our procedure for the preparation of 3-methylindole is superior to that using vapor-phase methanol over the CeHY catalyst.

Table 2
Ring-methylation of indole using vapor-phase methanol or supercritical methanol

Methanol	Indole conversion/%	3-Methylindole yield/%	3-Methylindole selectivity/%
Vapor-phase[a]	72.6	33.6	46.3
Supercritical[b]	89.9	74.2	82.5

[a] 573 K, 3 wt % CeHY catalyst, 1 h (Ref. 9).
[b] 623 K, no catalyst, 4 h.

2.3. Mechanism for methylation of indole using supercritical methanol

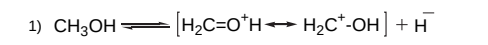
The methanol solutions of 5-methoxyindole, 5-bromoindole, and 5-chloroindole were subjected to reactions at 623 K for 1 h or 5 h. Table 3 shows the substituent effects on the conversion of the indoles using supercritical methanol. It is apparent that the electron-donating group ($-OCH_3$) somewhat accelerates the reaction, whereas the electron-attracting groups ($-Br$, $-Cl$) remarkably delay the reaction. This supports the idea that the methylation of indole using supercritical methanol is an electrophilic aromatic substitution and the methylating species acts as an electrophile.

Table 3
Substituent effects on the methylation of indoles with supercritical methanol

Indoles	Conversion/%	
	Reaction time 1 h	Reaction time 5 h
Indole	84	92
5-Bromoindole	8	34
5-Chloroindole	0	8
5-Methoxyindole	89	100

Reaction conditions: 0.10 mol dm^{-3} methanol solutions of indoles, 623 K.

We postulated the generation of R_2C^+-OH or $R_2C^{\delta+}-OH$ from the supercritical alcohol, R_2CH-OH.[11,12] The ionic species attacks at the C=C or C≡C bond as an electrophile to hydroxyalkylate the alkene or alkyne. For example, styrene gives rise to 3-phenylpropan-1-ol as a major product with supercritical methanol. For the supercritical methylation of indole, it can be presumed that the H_2C^+-OH acts as an electrophile (Scheme 1).



Scheme 1. Elimination of α-hydrogen of methanol.

The $[H_2C{=}O^+H \leftrightarrow H_2C^+{-}OH]$ can be also formed by the protonation of formaldehyde. The contribution of formaldehyde to the methylation of indole would be dependent on the concentration of the formaldehyde contaminant in the methanol. Brazaev et al. reported that supercritical methanol contains 5.16 wt % formaldehyde at 653 K.[13] Their result indicates that the oxidation of methanol to formaldehyde appreciably occurs under supercritical methanol conditions. In their experiments, it can be presumed that oxygen in the air and the surface of their reactor made of the EI-43BU-VD alloy containing Ni (77%) act as the oxidizing reagent and the oxidizing catalyst, respectively. On the other hand, in our experiments, all reactions were carried out in sealed Pyrex tubes. Most of the air in the tube was replaced by argon, and then the open end of the tube was sealed by the application of heat under reduced pressure. Thus, our reaction system contains very little air and nickel so that any formation of formaldehyde from the supercritical methanol should be negligible. Based on this view, we examined the amount of formaldehyde formed under our reaction conditions based on Nash's procedure.[14] Sample (A) was prepared by the simple distillation of commercial methanol (99.8%, Nacalai Tesque, Inc.). Sample (B) was prepared by maintaining sample (A) under our reaction conditions (623 K, in a sealed Pyrex reactor) for 3 h, followed by cooling to room temperature. Table 4 shows the formaldehyde concentration in the methanol samples.

Table 4
Determination of formaldehyde concentration in methanol

Methanol	Concentration of formaldehyde/mol dm^{-3}
A[a]	0.67×10^{-4}
B[b]	2.33×10^{-4}

[a] Methanol (A): prepared by a simple distillation of commercial methanol (99.8%, Nacalai Tesque, Inc.).
[b] Methanol (B): prepared by maintaining the sample (A) under the supercritical conditions (623 K, in a sealed Pyrex reactor) for 3 h., and then cooled to room temperature.

It appears that the amount of formaldehyde slightly increased at 623 K in the sealed Pyrex reactor, but the amount of formaldehyde in sample (B) is much less than that of indole in the reaction system. Thus, the formaldehyde in the reaction system would disappear during the very early stage of the methylation of indole so that the contribution of the contaminant formaldehyde to the methylation of indole would be negligibly small.

Takebayashi et al. proposed that H_3C^+ would be formed from the supercritical methanol and phenol ($CH_3OH+HOC_6H_5 \rightarrow CH_3O^+H_2+{}^-OC_6H_5$, $CH_3O^+H_2 \rightarrow CH_3^+ + H_2O$) during the *o*-methylation of phenol, and attack the *o*-position of the phenoxide.[5] However, in this study, the contribution of H_3C^+ to the supercritical methylation of indole would be negligibly small when compared to that of $[H_2C{=}O^+H \leftrightarrow H_2C^+{-}OH]$, because indole is much less acidic than phenol (pK_a of indole: 16.2, pK_a of phenol: 10.0). The main electrophile in the supercritical methylation of indole would be the $[H_2C{=}O^+H \leftrightarrow H_2C^+{-}OH]$.

As mentioned in Section 2.1, pyrrole is methylated in the presence of supercritical methanol, whereas 1-methylpyrrole is not methylated under the same conditions. In order to examine the reactivity of 1-methylindole in supercritical methanol, a 0.10 mol dm^{-3} methanol solution of 1-methylindole was subjected to reactions at 623 K. In the reaction system, no indol-1-ide (indole anion) and H^+ would be generated from 1-methylindole. Figure 3 shows the GC results of the reaction mixture at the reaction time of 5 h.

The peaks at around 1 and 7 min correspond to methanol and 1-methylindole, respectively. There are no peaks corresponding to materials other than the starting ones. This finding indicates that no methylation of 1-methylindole occurred at the C3 position and supports the idea that the dissociation of indole to indol-1-ide is essential for the methylation of indole at the C3 position.

Based on the idea that the reaction species for the supercritical methylation of indole are the indol-1-ide and H_2C^+-OH, (1*H*-indol-3-yl)methanol would be formed as follows (Scheme 2):

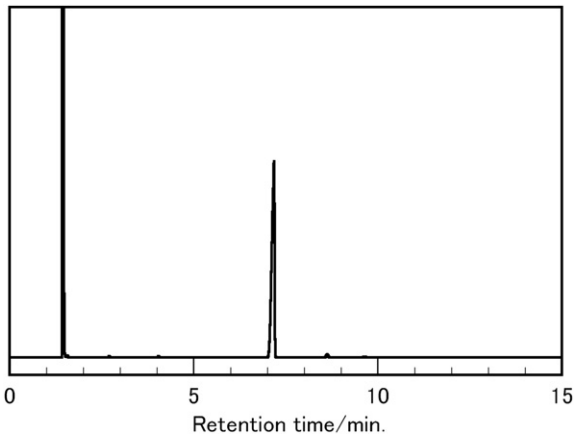
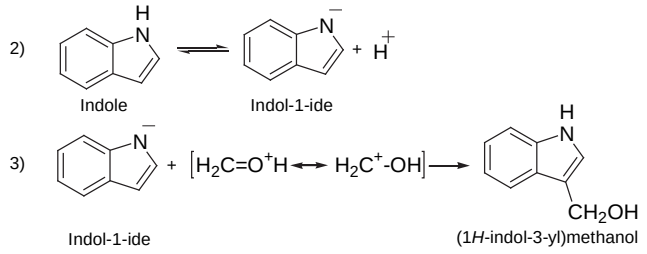


Figure 3. Attempts to methylate 1-methylindole using supercritical methanol: the GC of the reaction mixture. Initial concentration of 1-methylindole=0.10 mol dm^{-3}. Reaction temperature=623 K. Reaction time=5 h. the GC conditions: DB-17, 30-m column, 423 K, FID.



Scheme 2. Hydroxymethylation of indole.

However, we detected no formation of (1*H*-indol-3-yl)methanol in the GC–MS (UA-5, 30-m column, 373 K for 1 min→10 K rise/min to 523 K, the retention time of the authentic (1*H*-indol-3-yl) methanol: 10.8 min). There were no prominent peaks other than 3-methylindole (7.2 min) and 2,3-methylindole (8.5 min) in the reaction mixture. In order to examine the stability of (1*H*-indol-3-yl)methanol in supercritical methanol, a 0.120×10^{-4} dm^3 portion of the 0.010 mol dm^{-3} methanol solution of (1*H*-indol-3-yl)methanol was allowed to stand at 623 K for 1 h in a Pyrex reactor. The GC–MS of the reaction mixture was then measured. Figure 4 shows the GC of the authentic (1*H*-indol-3-yl)methanol and 3-methylindole, and the reaction mixture.

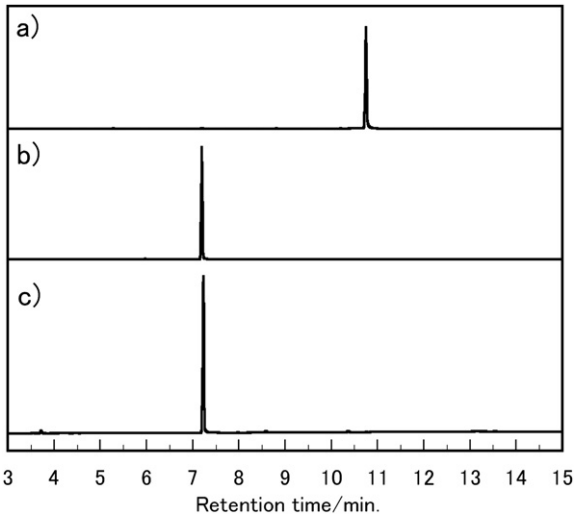
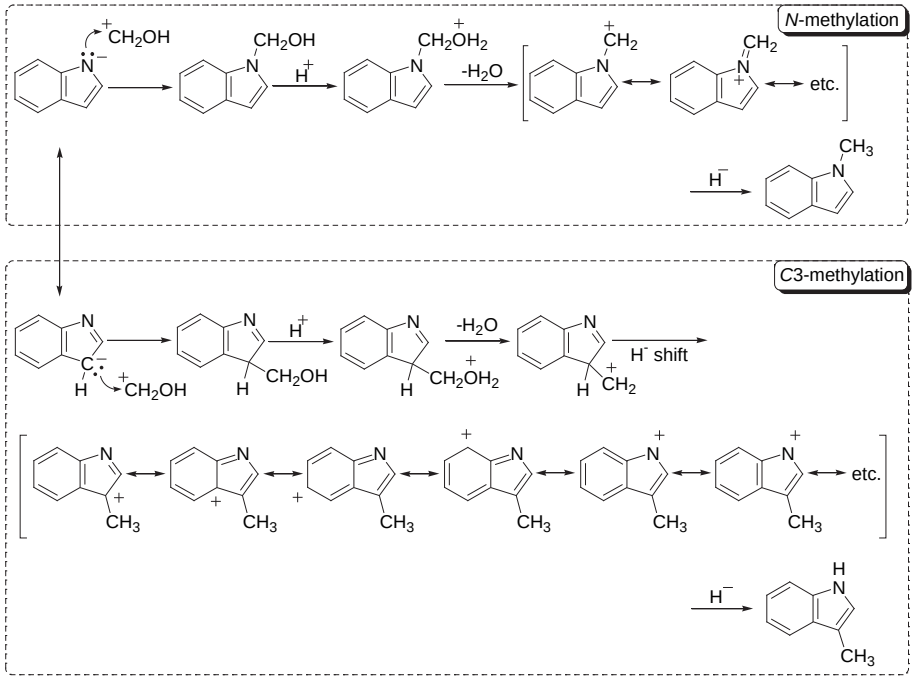


Figure 4. Reaction of (1*H*-indol-3-yl)methanol in supercritical methanol: the GC of authentic (1*H*-indol-3-yl)methanol, 3-methylindole, and the reaction mixture: (a) authentic (1*H*-indol-3-yl)methanol, (b) authentic 3-methylindole and (c) the reaction mixture. Initial concentration of (1*H*-indol-3-yl)methanol=0.010 mol dm^{-3}. Reaction temperature=623 K. Reaction time=1 h. The GC conditions: UA-5, 30-m column, 373 K for 1 min→10 K rise/min to 523 K, EI.

The (1*H*-indol-3-yl)methanol in the methanol solution disappears during the 1-h stand at 623 K. Moreover, the MS of the component with the GC peak at around 7.2 min agrees with that of the authentic 3-methylindole. Thus, it is reasonable to claim that the (1*H*-indol-3-yl)methanol is easily reduced to 3-methylindole under our experimental conditions. It can be assumed that the reaction proceeds as follows: the formation of a protonated alcohol intermediate→the dehydration to give a carbocation intermediate→the addition of a hydride ion to the carbocation intermediate (Scheme 3).



Scheme 3. Plausible pathway for the ring-methylation of indole using supercritical methanol.

As can be seen in Scheme 3, (1*H*-indol-1-yl)methanol produces a carbocation attached to the N atom of indole. The carbocation will be extremely unstable because the N atom bears a partial positive charge owing to resonance. On the other hand, (1*H*-indol-3-yl) methanol produces a rather stable tertiary carbocation through a hydride shift. The generated carbocation is more stable than ordinary tertiary ones because the charge is delocalized around the indole ring. The stability difference between the carbocations generated from the 1- and 3-hydroxymethylated indoles may be a reason why the supercritical methylation of indole occurs preferentially on the C3 instead of on the N1.

Supercritical methanol may act as the reducing reagent (hydride donor) for the reaction of (1*H*-indol-3-yl)methanol to 3-methylindole. It was reported that supercritical alcohols including methanol act as reducing reagents during the reduction of aldehydes or ketones to alcohols,[15–20] that of alkenes to alkanes and of diphenylacetylene to stilbene and dibenzyl.[11] Moreover, Hatano et al. reported that supercritical 2-propanol acts as a reducing reagent during the reduction of diarylmethanol to diarylmethane.[21] To the best of our knowledge, the reduction of (1*H*-indol-3-yl)methanol to 3-methylindole using supercritical methanol represents the first example of the reduction of monoaryl methanol to monoarylmethane using supercritical alcohol.

3. Conclusions

We examined the reactions of pyrrole or indole in the presence of supercritical methanol at 623 K. Ring-methylation of indole selectively occurred at the C3 position without the further addition of any catalyst, whereas pyrrole afforded the reaction mixture of the unreacted pyrrole and mono-, di-, tri-, and tetra-methylpyrroles. The supercritical ring-methylation of indole was assumed to proceed via (1*H*-indol-3-yl)methanol. The H_2C^+–OH generated from the supercritical methanol would attack the indol-1-ide at the C3 position to form (1*H*-indol-3-yl)methanol (electrophilic aromatic substitution), and then the (1*H*-indol-3-yl)methanol would be reduced to 3-methylindole in the presence of supercritical methanol.

4. Experimental

4.1. General

All reagents other than methanol were purchased from commercial sources and used without further purification. The methanol employed in the present investigation as the solvent and the ring-methylation reagent for the pyrrole or indole was purchased from a commercial source (99.8%, Nacalai Tesque, Inc.) and used after a simple distillation. The GC analyses were carried out using a Shimadzu GC-15A (DB-17 (J & W Scientific), 30-m column, FID) for the evaluation of the product distribution. The GC–MS spectra were obtained using a JEOL GC-mate II R (DB-5MS (J & W Scientific), 30-m column, EI) or a Shimadzu GCMS-QP2010 Plus (UA-5 (Frontier Lab), 30-m column, EI). The ^{1}H NMR spectra were measured using a Bruker DPX400. The UV–vis spectra were measured using a Shimadzu UV-3100.

4.2. Ring-methylation of pyrrole or indole using supercritical methanol

The reactions were carried out in sealed Pyrex tubes (ca. 0.02 dm inner diameter, ca. 0.70 dm length, and ca. 3.2×10^{-4} dm^3 inner volume). A 1.40×10^{-4} dm^3 (pyrrole) or 1.20×10^{-4} dm^3 (indole) portion of the methanol solution (the concentration of pyrrole or indole; specified in the text for each case) was placed in a Pyrex tube. The air in the tube was replaced by argon, and the open end of the tube was sealed by the application of heat under reduced pressure. After sealing, the tube was placed in an autoclave (SUS 316, 0.030 dm^3) with the appropriate amount of methanol. The methanol was used in order to prevent tube breakage as a result of any pressure difference. The autoclave was then heated to the reaction temperature (heating time from room temperature to 623 K: ~20 min). The reaction time mentioned in the text indicates the period when the vessel was maintained at the required reaction temperature. After a specific time, the autoclave was cooled using an air stream to quench the reaction (cooling time from 623 K to 473 K: ~10 min). The products in the tube were then identified using GC, ^{1}H NMR, GC–MS, and IR. Conversions were estimated by the GC analyses (DB-17) using the internal standard method.

4.3. Determination of formaldehyde in methanol

The amount of formaldehyde in the methanol employed in this study was determined by Nash's colorimetric procedure.[14] The color-producing solution was ammonium acetate (1.5 g) and 2,4-pentanedione (2.0×10^{-4} dm^3) dissolved in a small portion of water, and the aqueous solution made up to 0.10 dm^3 with water. The sample solution was a 2.5×10^{-4} dm^3 portion of the methanol made up to 0.10 dm^3 with water. The sample solution (5.0×10^{-3} dm^3) was placed in a screw-cap bottle together with the color-producing solution (5.0×10^{-3} dm^3). The bottle was warmed to 338 K in a water bath, and maintained at that temperature for 10 min. After cooling to room temperature, the amount of formaldehyde was colorimetrically determined at 412 nm.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.04.122.

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