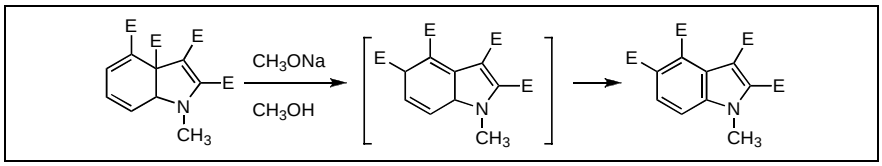
# Base-promoted Rearrangements of Ester Groups in 3a,7a-Dihydroindole-2,3,3a,4-tetraester



Kyu Ok Jeon, Ji Sook Yu, and Chang Kiu Lee*

Department of Chemistry, Kangwon National University, Chuncheon 200-701 Korea
cklee410@kangwon.ac.kr

Received November 3, 2006




Tetramethyl 3a,7a-dihydro-1-methyl-1*H*-indole-2,3,3a,4-tetracarboxylate which is an 1:2 adduct of 1-methylpyrrole and dimethyl acetylenedicarboxylate underwent isomerization catalyzed by sodium methoxide to form a 5,7a-dihydro-1-methyl-1*H*-indole-2,3,4,5-tetracarboxylate, its 5,6-dihydro isomer, and a ring opening product which is an azonine derivative. Fully aromatized esters such as 1-methylindole-2,3,4-triester, 1-methylindole-2,3,4,5-tetraester and 1-methyl-2,3,4,6-tetraester were also isolated. An indole compound which could be formed by conjugative addition of the methoxide ion was also isolated.

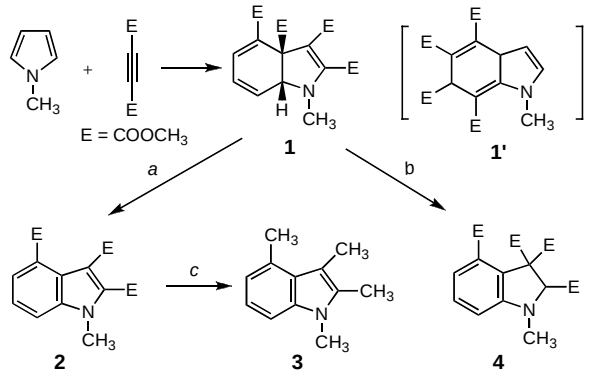
*J. Heterocyclic Chem.*, **44**, 1115 (2007).

## INTRODUCTION

One of the synthetic approaches to an indole skeleton is the formation of the 3a,7a-dihydroindole moiety from the reactions of *N*-substituted pyrroles with dimethyl acetylenedicarboxylate (DMAD). The method seems to be useful because 1) the yields are usually high (80-90%); 2) the dihydroindoles can be readily converted to indoles almost quantitatively; and 3) the ester group can be transformed to various functional groups.

The reaction of 1-methylpyrrole with DMAD was first reported by Diels, Alder, and Winkler with an incorrect structure (**1'**) for the 1:2 adduct [1]. With aid of NMR spectroscopy Acheson and Vernon reported **1** as the correct structure [2]. The positions of the four ester groups were conformed by the oxidation of **1** with bromine in methanol to **2** which is a fully aromatized indole derivative. The indole triester **2** was transformed to 1,2,3,4-tetramethylindole (**3**), which is identical with the compound prepared by methylation of known 2,3,4-trimethylindole [3]. Therefore, the positions of the ester groups are unambiguous (Scheme 1).

**Scheme 1**

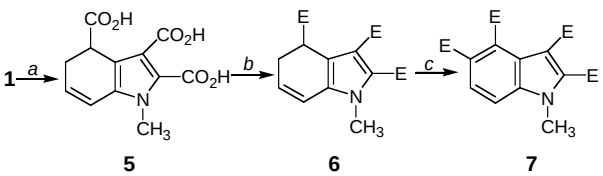



(a) $Br_2$/MeOH; (b) Pd-C, 140 $^oC$, 10min (4%) or xylene, reflux 24 h (74%); (c) $LiAlH_4$, $AlCl_3$

X-ray crystallographic study of **1** shows that the five- and six-membered rings are *cis*-fused and, therefore, 3a-$COOCH_3$ group and 7a-H are *cis* [4]. The dihedral angle of *N*-$CH_3$ group and 7a-H are close to 90°, which may be an indication that the conjugation of the lone pair electron on the N atom through 2-C–3-C and 3-C–O double bonds is significant. Such kind of conjugation, in addition to the aromatization of the dihydrobenzene ring, may be the driving force of the rearrangement of the 3a-$COOCH_3$ group to 3-position forming a 2,3-dihydroindole-2,3,3,4-tetraester **4** upon heating with 5% palladium-charcoal for 10 min (4%) [5] or refluxing in xylene for 24 h (74%) [3].

On the other hand, **1** was converted to **7** when refluxed with sodium methoxide in methanol for 24 h in 14% yield [3]. Compound **7** was also prepared by Acheson and Vernon by a different method: hydrolysis of **1** with potassium hydroxide to 4,5-dihydro-1-methylindole-2,3,4-tricarboxylic acid (**5**), followed by treatment with diazomethane to form the triester **6**, and then reacting with DMAD at 200 ℃ for 1.5 h to give **7** (6% from **6**) as shown in Scheme 2 [6].

**Scheme 2**




(a) KOH/$H_2O$/MeOH; (b) $CH_2N_2$; (c) DMAD

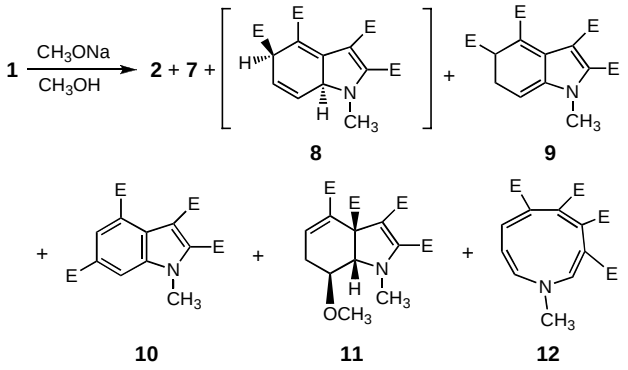
Formation of the tetraester **7** directly from **1** by sodium methoxide should involve a rearrangement of the 3a-

$COOCH_3$ group and dehydrogenation. The dehydrogenation may not be surprising because the resulted product is a fully aromatic indole compound. However, the rearrangement of the ester group to 5-position is quite unique. The mechanism seems to deserve investigation. Furthermore, the tetraester may be converted to various functional groups serving as a useful intermediate for the synthesis of polycyclic compounds having indole skeleton at their core.

## RESULTS AND DISCUSSION

When the dihydroindole ester **1** was heated at reflux with an equimolar amount of sodium methoxide in methanol for 24 h and cooled slowly, colorless needles of **7** precipitated. The yield of **7** varied depending on the reaction time, the concentration, and the molar ratio of **1** and sodium methoxide. The best yield of **7** was about 30% when a 1:1 molar ratio solution of the substrate and the base was refluxed for 48 h under a gentle stream of oxygen gas. The filtrate after removal of **7** was chromatographed on a column of silica gel eluting with a 1:1 hexane-ethyl acetate mixture to give, in addition to more of **7**, other esters such as **2**, **9**, **10**, **11**, and **12** (Scheme 3).

**Scheme 3**

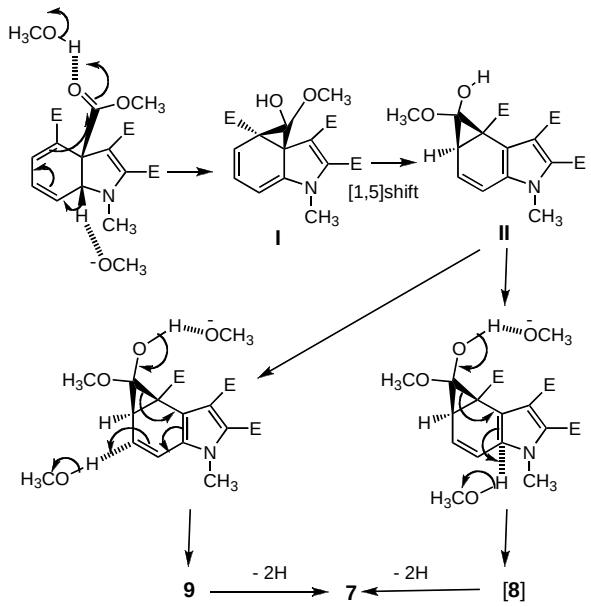



The progress of the reaction was monitored by NMR spectroscopy and the results are listed in Table 1. The $^1H$ and $^{13}C$ chemical shift values are listed in Tables 2 and 3, respectively. It should be pointed out that no change in **1** was observed when a solution of it in methanol was refluxed for 2 days. Therefore, the formation of the isomeric esters from **1** should be caused by sodium methoxide. As shown in Table 1 about 60% of **1** was transformed to **8** within one hour of reflux and reached about 76% after 6 h. Pure form of **8** was isolated by column chromatography as a gummy material, but various attempts to make a solid form was unsuccessful. Once separated from other components by chromatography the compound **8** gradually transformed to **7** and **2**. We were able to obtain a high resolution mass spectrum of **8** (calcd for $C_{17}H_{19}NO_8$: 397.1111; found: 365.0985), but it is not certain whether the compound was changed after isolation.

The structure of **8** was established by $^1H$ NMR spectroscopy. A singlet corresponding to *N*-$CH_3$ appears at δ 3.02, which is an indication that the heterocyclic ring is not fully aromatic. The singlet of *N*-$CH_3$ in an indole ester usually appears at around δ 4. There are two doublets at δ 4.38 ($J$ = 6.3 Hz) and 5.10 ($J$ = 5.7 Hz) for 5-H and 7a-H, respectively. There are two signals (a doublet of doublets) at δ 5.48 and 6.07 with a common coupling constant of 9.4 Hz and different values of 6.3 and 5.7 Hz, respectively. Therefore, it seems reasonable to assign the peak at δ 5.48 to the 6-H and δ 6.07 to the 7-H.

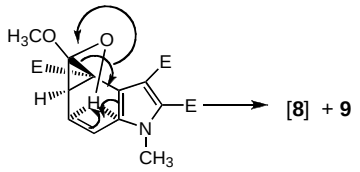
The close values of the coupling constants of $J_{5,6}$ and $J_{7,7a}$ may be an indication that the dihedral angles of 5-H–5-C—6-C–6-H and 7-H–7-C—7a-C–7a-H are of very similar magnitude. In order to achieve the close dihedral angles the 5-H and 7a-H should occupy the axial positions of 1,4-cyclohexadiene ring. The conformation may be readily understood by the proposed mechanism for the formation of **8** from **1** as shown in Scheme 4. The methoxide ion seems to abstract the 7a-H first and the intermediate **I** forms to give conjugation. The [1,5] suprafacial shift of the cyclopropane ring would result in formation of **II**. Ring opening should be assisted by both the methoxide ion and methanol, which are approaching from the opposite sides of the indole plane. Therefore, the H atoms at 5-C and 7a-C should be on the same side, and consequently, the dihedral angles should have close values.

**Scheme 4**




Dehydrogenation of **8** to **7** seems to be facilitated by an oxygen molecule although the mechanism is not certain. The yield of **7** was increased from ~10% to ~30% by purging with oxygen gas during the reflux. The transfor-

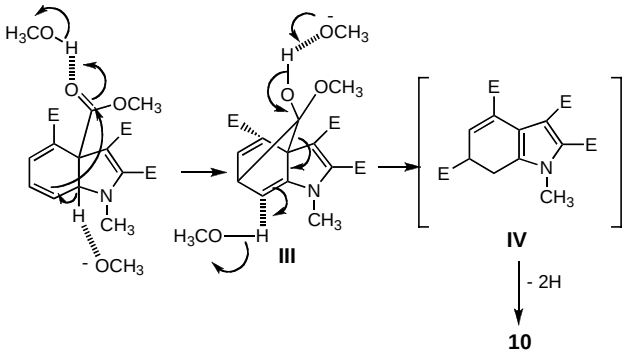
mation of **1** to **7** seems to compete with another process such as formation of **9**. An intermediate like **II** may be involved in the formation of **8** and **9**. They differ only in the positions of protonation: that is, at 7a-C for **8** and 6-C for **9** (Scheme 4). Alternatively, we cannot rule out the intramolecular transfer of the proton through a six-membered ring transition state as below:




The $^1$H-NMR spectrum of **9** shows a triplet and a doublet of doublets at δ 3.45 and 3.49, which should correspond to the methylene protons at 6-C. Both 5-C and 6-C are $sp^3$-hybridized, which was confirmed by significant up field shift to 40.36 and 24.25 ppm, respectively, in its $^{13}$C-NMR spectrum. The $^1$H-$^{13}$C HETCOR spectrum clearly shows the correlation of a triplet at δ 4.90 with the peak at 40.35 ppm and the peaks at δ 3.45 and 3.49 to the carbon signal at 24.25 ppm.

Although the formation of **I** should be kinetically favorable, an alternative bicyclic intermediate **III** formed as the result of a minor pathway (Scheme 5).

**Scheme 5**

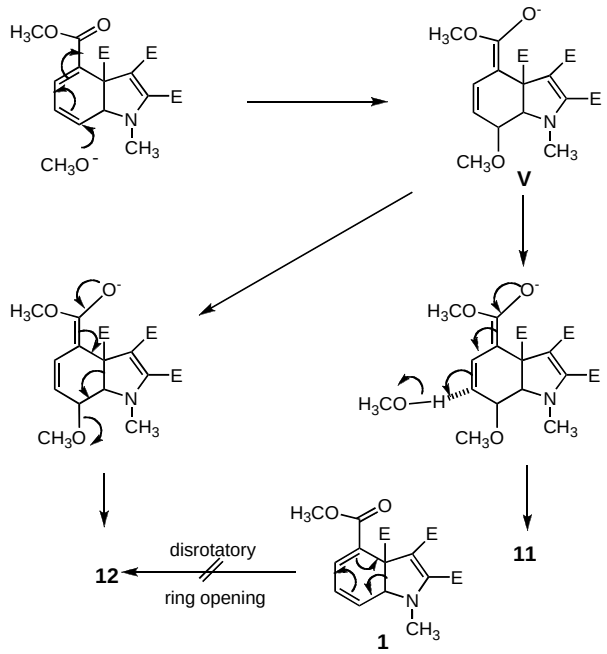



The ring opening of **III** should give a 6,7-dihydroindole tetraester **IV** although it was not isolated. Instead a fully aromatized indole ester **10** was isolated in 3% yield. It is conceivable that the intermediate **IV** was oxidized by air to form **10**. The structure of **10** was determined readily by NMR spectroscopy. Its $^1$H NMR spectrum consisted of seven singlets: five of 3Hs ($CH_3$, four $COOCH_3$) and two of 1H. The singlets at δ 6.85 and 6.99 are a clear indication that the ester groups are at 4- and 6-positions of the indole ring.

The methoxide ion also underwent addition to the conjugate carbonyl system as shown in Scheme 6.

The portion of the six-membered ring of the 3a,7a-dihydroindole ester is an α,β,γ,δ-unsaturated ester.

**Scheme 6**




Therefore, a nucleophile (methoxide ion in this case) can add to the δ-carbon to form an intermediate **V** as shown in Scheme 6. The formation of intermediate **V** seemed to proceed by two pathways: completion of the addition by accepting a proton at γ-position from the solvent to form **11** and ring opening to result in **12**.

The structure of **11** was also established by 2D-NMR spectroscopy. The five singlets corresponding to the methoxy groups definitely suggest the addition of methanol to a C–C double bond of **1**. The high resolution mass spectrum also confirmed the molecular formula. The two sets of proton peaks at δ 2.35 (ddd) and 2.59 (dt) were correlated to a carbon peak at 27.71 ppm. Both H and C chemical shift values are unambiguously corresponding to a $sp^3$-hybridized carbon atom. Furthermore, a doublet of doublets at δ 4.04 (7-H) and a doublet at δ 3.94 (7a-H) with a coupling constant of 3.6 Hz may indicate that the methoxide ion is approaching from the same side of 7a-H so that 7-H and 7a-H are in the gauche arrangement with a dihedral angle close to 90°. These observations are consistent with the structure **11**.

One of the most interesting observations from the reaction of sodium methoxide and **1** is the methoxide-catalyzed ring opening of **1** to form **12**. The electrocyclic reaction theory may readily explain the pathway as a disrotatory electrocyclic reversion in which six electrons are involved. Therefore, it is a thermally-allowed process in the ground state [7]. The electrocyclic ring opening of bicyclic compounds involving fused three- or four-membered rings is common [8]. However, there is no reported example of a 3a,7a-dihydroindole opening to a

nine-membered ring of a 1-azacyclonona-2,4,6,8-tetraene (1*H*-azonine) derivative, to the best of our knowledge, although the reverse process have been reported [9]. The azonine ester **12** can be considered as a heterocyclic aromatic compound that has ten electrons (eight electrons of four C–C double bonds and two electrons of the lone pair on the N atom) according to the Hückel's rule of aromaticity. As mentioned earlier, refluxing in methanol did not affect **1**. Refluxing in xylene caused the rearrangement of 3a-$COOCH_3$ to the 3-position to form **4** (Scheme 1). Therefore, the presence of methoxide ion should be essential in ring opening. This means that the formation of **12** is not a direct result of electrocyclic reversion. An alternative mechanism may be involved as shown in Scheme 6.

Unlike the spectra of the dihydroindole esters of which the signals of *N*-$CH_3$ appear around δ 2.8-3.0 those of **12** appears at δ 3.84 which is a typical value for the chemical shift of *N*-methylindole esters. The down field shift should be due to the aromatic nature of the 1*H*-azonine ester. The chemical shifts and splitting patterns of the 6-, 7-, 8-, and 9-Hs are also consistent those of typical aromatic compounds. The $^1$H spectrum shows two triplets at δ 6.38 (8-H) and 7.85 (7-H) and two doublets at δ 5.82 (6-H) and 6.69 (9-H). The coupling constants are 11.6 ($J_{7,8}$), 11.5 ($J_{8,9}$), and 11.4 ($J_{6,7}$) Hz. The values are slightly larger than the typical *ortho* coupling constants of benzene derivatives (usually 7-10 Hz) [10], but it may not be surprising considering that the nine-membered ring may not be completely planar [8]. When the signals are expanded, there is noticeable *meta*- and *para*-coupling and the triplets are split into a triplet of doublets and the doublets are split into a doublet of triplets. The *meta* and *para* coupling constants are about 0.9-1.1 Hz. The close values of the *meta*- and *para*-coupling constants may be an indication that the nine-membered ring is not coplanar. Instead, the 6-H and 9-H are slightly out of the plane so that the *para*-coupling is more effective.

Not only do the values of the $^1$H chemical shifts reflect the protons being on a $sp^2$-C but the value of the chemical shifts of $^{13}$C that appear around 112-139 ppm clearly support the idea that the ring carbon atoms of **12** are all $sp^2$-hybridized. There is no signal that may be considered the result of an $sp^3$-hybridized C-H group.

Another noteworthy reaction of **1** induced by methoxide ion is aromatization to **2**. Compound **2** is readily formed by treatment of **1** with bromine in methanol and has been well characterized [2,3]. However, the base-induced aromatization seems quite unique, although the fate of 3a-$COOCH_3$ group is not certain. A plausible mechanism for the aromatization may be represented as shown in Scheme 7. The yield of **2** from **1** after reflux for 24 h was about 20%.

**Scheme 7**

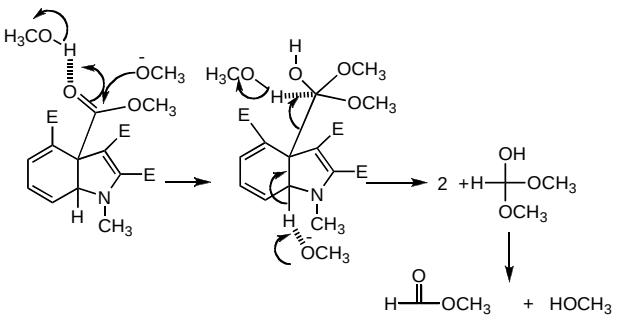


**Table 1**

Relative Percentages of the Compositions of the Various Esters Determined by NMR Spectroscopy

| Time | **1** | **2** | **7** | **8** | **11** | **12** |
|---|---|---|---|---|---|---|
| 0 h | 100 | 0 | 0 | 0 | 0 | 0 |
| 1 h | 26.6 | 3.3 | 0.1 | 61.3 | 6.6 | 2.1 |
| 2 h | 12.1 | 5.7 | 0.2 | 70.0 | 8.5 | 3.5 |
| 4 | 4.6 | 8.6 | 0.2 | 74.4 | 9.4 | 2.8 |
| 6 h | 0 | 10.5 | 1.7 | 75.6 | 9.6 | 2.6 |
| 12 h | 0 | 13.3 | 5.6 | 67.8 | 12.3 | 1.0 |
| 24 h | 0 | 21.1 | 28.9 | 17.9 | 32.0 | 0 |

## EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra in chloroform-d solution were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for $^1$H and 100 MHz for $^{13}$C and were referenced to tetramethylsilane. Infrared spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Mass spectra were obtained using a Micromass Autospec M363 in the Central Lab of Kangwon National University. The ionization conditions were 60 °C and 70 eV.

1-Methylpyrrole and DMAD were obtained as the commercial products and were distilled prior to use. Column chromatography was performed using silica gel and 1:1 mixture of ethyl acetate and hexane as elution solvent.

Reaction of **1** with Sodium Methoxide in Methanol. A solution of **1** (1.00 g, 2.7 mmoles) and sodium methoxide (0.29 g, 5.4 mmoles) in dried methanol (50 mL) was heated at reflux for 27 h. After cooling, the precipitate was collected by filtration and recrystallized from methanol to give **7** (0.21 g, 21%), mp 197 ℃ (lit. [2] 200 ℃). The filtrate was chromatographed to give **2**, **10**, and **11**.

**Trimethyl 1-Methyl-(*1H*)-indole-2,3,4-tricarboxylate (2)**. Colorless prism, 0.11 g, 13%, mp 124-125 ℃ (lit. [2] 124 ℃).

**Tetramethyl 1-Methyl-(*1H*)-indole-2,3,4,6-tetracarboxylate (10)**. This compound was obtained as a semi solid, <0.01 g, <1%, mp uncertain; MS m/z (%): 363 (35, $M^+$), 332 (100, $M^+$ - $CH_3O$); HRMS calcd for $C_{17}H_{17}NO_8$: 363.0954. Found: 363.0829.

**Tetramethyl 6,7-Dihydro-7-methoxy-1-methyl-(1*H*)-indole-2,3,3a,4-tetracarboxylate (11)**. White solid, 0.06g, 6%, mp 133-135 ℃; IR (KBr) 2953 w, 2900 vw, 1753, s, 1728 vs, 1677

**Table 2**

$^1$H Chemical Shift Values (δ) of the Tetraesters in Chloroform-*d* (*J* in Hz)

| Position | **1** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|
| *N*-$CH_3$ | 2.79 s | 3.90 s | 3.02 | 3.64 s | 3.87 s | 2.84 s |
| 2-$OCH_3$ | 3.62 s[a] | 3.92 s[a] | 3.60 s[a] | 3.77 s[a] | 3.87 s[a] | 3.63 s[a] |
| 3- $OCH_3$ | 3.76 s[a] | 3.96 s[a] | 3.67 s[a] | 3.80 s[a] | 3.95 s[a] | 3.72 s[a] |
| 3a-$OCH_3$ | 3.90 s[a] | - | - | - | - | 3.89 s[a] |
| 4- $OCH_3$ | 3.80 s[a] | 3.98 s[a] | 3.71 s[a] | 3.83 s[a] | 3.96 s[a] | 3.77 s[a] |
| 5-H | 7.03 d | 3.99 s[a] | 3.95 s[a] | 3.90 s[a] | 6.85 s | 6.87 t |
| | $J_{5,6}$ = 5.9 | | 4.38 d | 4.90 t | | $J_{5,6}$ = 4.2 |
| | | | $J_{5,6}$ = 6.0 | $J_{5,6}$ = 4.7 | | |
| 6-H | 6.26 ddd | 8.00 d | 5.48 dd | 3.45 t | 4.08 s[a] | 2.35ddd |
| | $J_{6,5}$= 5.9 | $J_{6,7}$ = 8.9 | $J_{6,5}$= 6.3 | 3.49 dd | | 2.59dt |
| | $J_{6,7}$ = 9.7 | | $J_{6,7}$ = 9.4 | $J_{6,5}$= 4.6 | | $J_{6,5}$= 4.5 |
| | $J_{6,7a}$=1.1 | | | $J_{6,7}$ = 3.5 | | $J_{6,7}$= 5.7 |
| | | | | | | $J_{6\alpha,6\beta}$=18.6 |
| 7-H | 5.97 dd | 7.48 d | 6.07 ddd | 7.31 t | 6.99 s | 4.04 dd |
| | $J_{7,6}$ = 9.7 | $J_{7,6}$ = 8.9 | $J_{7,6}$ = 9.4 | $J_{7,6}$ = 3.6 | | $J_{7,6}$ = 5.7 |
| | $J_{7,7a}$=3.7 | | $J_{7,7a}$=5.7 | | | $J_{7,7a}$ = 3.6 |
| 7a-H | 4.83 dd | - | 5.10 d | | | 3.94 d |
| | $J_{7a,7}$=3.7 | | $J_{7a,7}$=5.6 | | | $J_{7a,7}$ = 3.6 |
| | $J_{7a,6}$=1.1 | | | | | |

[a] Singlet corresponding to $OCH_3$ of the ester group and the assignment is uncertain.

**Table 3**

$^{13}$C Chemical Shift Values (ppm) of the Tetraesters in Chloroform-*d*

| Position | **1** | **7** | **9** | **10** | **11** |
|---|---|---|---|---|---|
| *N*-$CH_3$ | 32.01 | 32.07 | 32.80 | 34.79 | 34.83 |
| 2-$OCH_3$ | 152.84 | 131.71 | 128.39 | 133.67 | 153.28 |
| | 51.72[a] | 52.38[a] | 51.19[a] | 52.51[a] | 52.24[a] |
| | 163.89[b] | 161.52[b] | 166.26[b] | 164.72[b] | 163.57[b] |
| 3- $OCH_3$ | 103.06 | 120.53 | 112.57 | 121.86 | 105.34 |
| | 50.83[a] | 52.53[a] | 52.13[a] | 52.27[a] | 51.49[a] |
| | 162.99[b] | 164.65[b] | 161.10[b] | 161.68[b] | 164.39[b] |
| 3a- $OCH_3$ | 55.05 | 113.43 | 120.39 | 111.82 | 56.24 |
| | 53.01[a] | | | | 53.44[a] |
| | 174.27[b] | | | | 173.71[b] |
| 4- $OCH_3$ | 126.66 | 122.18 | 122.14 | 122.75 | 129.96 |
| | 52.74[a] | 52.61[a] | 52.44[a] | 52.85[a] | 53.30[a] |
| | 166.03[b] | 166.46[b] | 165.90[b] | 166.39[b] | 167.30[b] |
| 5-C | 130.82 | 130.18 | 40.36 | 143.96 | 136.54 |
| | | 52.83[a] | 51.79[a] | | |
| | | 168.11[b] | 171.69[b] | | |
| 6- C | 123.36 | 126.23 | 24.25 | 123.09 | 27.71 |
| | | | | 52.80[a] | |
| | | | | 169.68[b] | |
| 7- C | 125.08 | 111.34 | 135.83 | 111.45 | 74.24 |
| | | | | | 57.31[a] |
| 7a- C | 70.69 | 139.55 | 130.66 | 129.10 | 73.02 |

[a] Signal corresponding to $OCH_3$ and the assignment is uncertain. [b] Signal corresponding to C=O and the assignment is uncertain.

s, 1588 ms, 1441 ms, 1346 ms, 1240 vs, 1149 s, 1104 m, 1041 m, 1000 m; MS m/z (%): 397 (5, $M^+$), 366 (5, $M^+$ - $CH_3O$), 338 (14, $M^+$ - $CH_3OCO$), 306 (100, $M^+$ - $CH_3O$ - $CH_3OCOH$), 278 (25), 246 (95, $M^+$ - $CH_3O$ - $2CH_3OCOH$); HRMS calcd for $C_{18}H_{23}NO_9$: 397.1373. Found: 397.1355. Anal. Calcd for $C_{18}H_{23}NO_9$ (397.38): C, 54.40; H, 5.83; N, 3.52. Found: C, 54.68; H, 5.52; N, 3.54.

A similar reaction was performed with **1** (0.50 g, 1.4 mmole) and sodium methoxide (0.15 g, 2.8 mmoles) in methanol (20 mL) for 16 h. The solvent was evaporated off and the residue was fractionally crystallized from methanol to give **9** and **12**.

**Tetramethyl 5,6-Dihydro-1-methyl-(1*H*)-indole-2,3,4,5-tetracarboxylate (9)**. White solid, 0.13 g, 26%, mp 172-175 °C; IR (KBr) 2997 vw, 2955 w, 1740 s, 1704 vs, 1442 m, 1394 mw, 1264 9vs, 1224 s, 1175 s, 1113 m, 985 m; MS m/z (%): 365 (11, $M^+$), 334 (21, $M^+$ - $CH_3O$), 274 (100, $M^+$ - $CH_3O$ - $CH_3OCOH$); HRMS calcd for $C_{17}H_{19}NO_8$: 365.1111. Found: 365.1286. Anal. Calcd for $C_{17}H_{19}NO_8$ (365.33): C, 55.89; H, 5.24; N, 3.83. Found: C, 55.67; H, 5.32; N, 3.66.

**Tetramethyl 1-Methyl-(1*H*)-azonine-2,3,4,5-tetracarboxylate (12)**. This compound was obtained as a semi solid, 0.14 g, 27%; IR (neat) 3001 w, 2952 m, 2842 w, 1745 s, 1709 vs, 1439 ms, 1389 m, 1256 s, 1219 vs, 1175 s, 1112 s, 1072 s, 997 m; MS m/z (%): 365 (13, $M^+$), 334 (28, $M^+$ - $CH_3O$), 333 (39, $M^+$ - $CH_3OH$), 274 (100, $M^+$ - $CH_3O$ - $CH_3OCOH$); HRMS calcd for $C_{17}H_{19}NO_8$: 397.1111. Found: 365.0998. Anal. Calcd for $C_{17}H_{19}NO_8$ (365.33): C, 55.89; H, 5.24; N, 3.83. Found: C, 55.58; H, 5.45; N, 3.61.

**Acknowledgement.** We thank Dr. Gary Kwong of the 3M Co. for help in preparing the manuscript. This research was supported by Korea Research Foundation (KRF-2003-005-C00021).

## REFERENCES AND NOTES

[1] Diels, O.; Alder, K.; Winkler, H. *Annalen* **1931**, *490*, 267.
[2] Acheson, R. M.; Vernon, J. M. *J. Chem. Soc.* **1962** 1148.
[3] Lee, C. K.; Hahn, C. S.; Noland, W. E. *J. Org. Chem.* **1978**, *43*, 3727.
[4] Kang, Y. J. private communication.
[5] Acheson, R. M.; Vernon, J. M. *J. Chem. Soc.* **1963** 1907.
[6] Acheson, R. M. *J. Chem. Soc.* **1965** 2630.
[7] Fleming, I. *Pericyclic Reactions*, Oxford Scienc Pub., **1999**, pp 57-69.
[8] Anastassiou, A. G. *Acc. Chem. Res.* **1972**, *5*, 281.
[9] Anastassiou, A. G.; Gebrian, J. H. *Tetrahedron Lett.* **1970** 825.
[10] Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy*, 3rd Ed., Harcourt College Pub., Fort Worth, p. 261.