# PREPARATION OF NOVEL CYCLIC HYPERVALENT IODINE(III) COMPOUNDS HAVING AZIDO, CYANO, AND NITRATO LIGANDS†

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**Abstract** – The title cyclic hypervalent iodine compounds (**4-8**) were prepared in good yields by the ligand exchange reaction of the acetoxy cyclic iodinanes (**1-3**) with trimethylsilyl compounds and of the chloro cyclic iodinane (**9**) with silver nitrate, and were found to be air-stable at room temperature.

Recently, hypervalent iodine(III) compounds have been extensively used in organic syntheses due to their low toxicity, ready availability, and easy handling.[1] Most of the reported isolable reagents have electron negative halogen or oxygen ligands such as chloro, fluoro, acyloxy, hydroxyl, and sulfonyloxy ligands and were useful for the introduction of their ligands to a variety of substrates through an oxidation step. Therefore, preparation of iodinanes having novel ligands will enlarge the utilities of hypervalent iodine compounds in synthetic organic chemistry. Although the reagents having one or two azido ligands have been prepared from phenyliodine diacetate or iodosobenzene and TMS-$N_3$, and used for the azidation of various compounds, they are too labile to be isolated and even to be identified by spectroscopic means.[2] Reagents having cyano ligands were prepared; however, they are not very stable and must be handled under a nitrogen atmosphere.[3] We wish to present here the preparation of the cyclic iodinanes (**4-8**) having azido, cyano, and nitrato ligands, which are crystalline compounds and air-stable at room temperature.[4,5]

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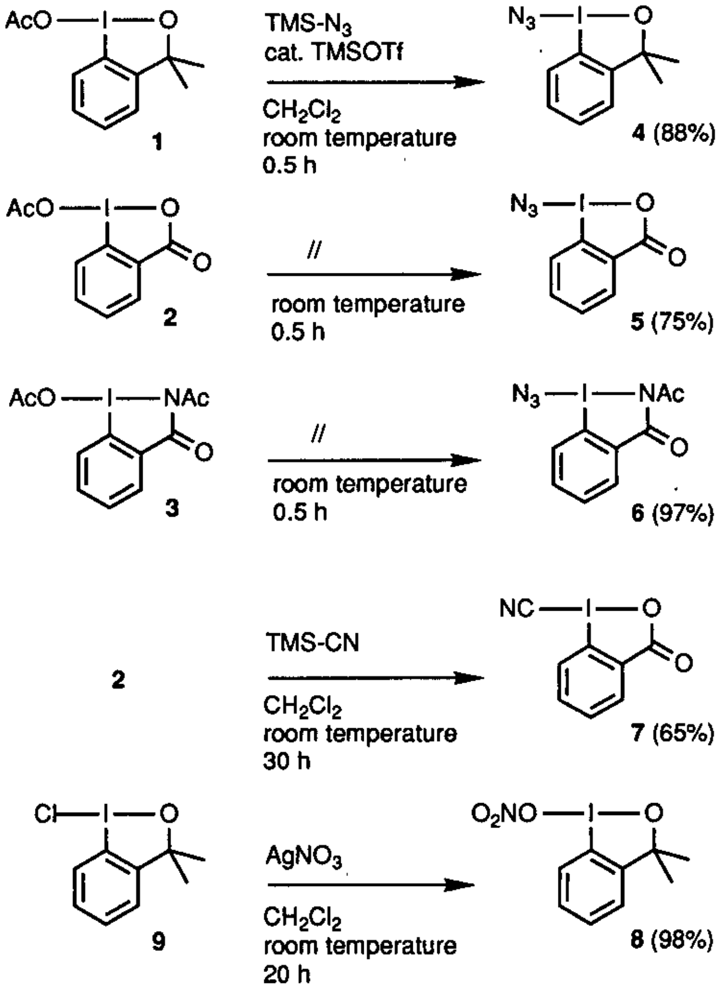
† This paper is dedicated to the memory of the late Professor Yoshio Ban.

Although the ligand exchange reaction of phenyliodine diacetate or iodosobenzene with TMS-$N_3$ was reported to proceed even at -78 °C,[2] the reaction of acetoxy cyclic iodinane (**1**) with 1.5 eq. of TMS-$N_3$ in $CDCl_3$ was sluggish at room temperature and finally gave a complex mixture. However, the addition of *ca.* 0.005 eq. of TMSOTf accelerated the reaction to provide the expected novel reagent (**4**) in nearly quantitative yield based on $^1H$ nmr analysis. Practically, the reaction was carried out in dry $CH_2Cl_2$ at room temperature for 0.5 h and the reaction mixture was concentrated in vacuo to give a precipitate, which was washed with hexane to give **4** (88% isolated yield) as pale yellow crystals (Scheme 1). Compound (**4**), prepared in this manner, was stable enough to handle in air without any problems. Using a similar procedure, the reactions of **2** or **3** with TMS-$N_3$ gave the corresponding azido compounds (**5** and **6**) in 75% and 97% isolated yields, respectively. The structures of these products (**4-6**) were unambiguously identified by ir, $^1H$ and $^{13}C$ nmr, and mass spectroscopic data as well as microanalyses and/or high resolution mass spectroscopies (Table 1). Especially, the ir data showed the characteristic absorption of the azido groups between 2029 and 2070 $cm^{-1}$. $^1H$ Nmr data had the typical four aromatic signals of the *ortho*-disubstituted benzene rings. $^{13}C$ Nmr data showed typical signals (δ 113.9-115.9) of the carbons substituted with trivalent iodine.[4c]

In a like manner, the ligand exchange reaction of **2** with TMS-CN occurred, but without TMSOTf, to give the corresponding cyclic compound (**7**) having a cyano ligand. This compound was also isolated as colorless crystals in 65% yield and was fully characterized (Table 1).



Scheme 1

Table 1. Physical and Spectral Data for Cyclic Iodinanes (**4**-**8**).[a]

| Compound | mp, °C (solvent) | Ir (KBr), $cm^{-1}$ | $^1H$ Nmr ($CDCl_3$), $\delta$ | $^{13}C$ Nmr ($CDCl_3$), $\delta$ | EI Mass, m/z |
|---|---|---|---|---|---|
| **4** | 112-114.5 ($CH_2Cl_2$-hexane) | 2029 ($N_3$) | 1.53 (6 H, s), 7.23 (1 H, dd, *J*=7.0, 2.0 Hz), 7.49-7.59 (2 H, m), 7.77 (1 H, dd, *J*=7.5, 1.5 Hz) | 149.1, 130.8, 130.2, 127.7, 126.6, 113.9 (Ph), 83.1 (*C*Me$_2$), 29.5 (Me$_2$) | 261 ($M^+$-$N_3$) |
| **5** | ≥135 (decomp.) | 2070 ($N_3$), 1665 (CO) | 7.79 (1 H, td, *J*=7.5, 1.5 Hz), 7.95-8.05 (2 H, m), 8.27 (1 H, dd, *J*=7.5, 1.5 Hz)[b] | 166.8 (CO), 135.4, 132.4, 130.9, 125.9, 117.2, 115.9 (Ph)[b] | 247 ($M^+$-$N_3$) |
| **6** | 184-186 (AcOEt) | 2056 ($N_3$), 1684 (CO), 1632 (NAc) | 2.65 (3 H, s), 7.77 (1 H, t, *J*=7.5 Hz), 7.93 (1 H, td, *J*=7.5, 2.0 Hz), 8.16 (1 H, d, *J*=7.5 Hz), 8.26 (1 H, dd, *J*=7.5, 2.0 Hz) | 176.6 (NAc), 161.5 (CO), 136.5, 134.5, 132.4, 131.5, 128.0, 114.9 (Ph), 25.8 (Me) | 288 ($M^+$-$N_3$) |
| **7**[c] | 155-158 (AcOEt) | 2161 (CN), 1636 (CO) | 7.90 (1 H, t, *J*=7.5 Hz), 8.03 (1 H, td, *J*=7.5, 1.5 Hz), 8.14 (1 H, dd, *J*=7.5, 1.5 Hz), 8.31 (1 H, d, *J*=7.5 Hz)[d] | 167.3 (CO), 137.1, 132.6, 132.5, 130.8, 128.4, 118.0 (Ph), 88.5 (CN)[d] | 273 ($M^+$) |
| **8** | 172-174.5 ($CH_2Cl_2$-hexane) | 1497, 1277 ($ONO_2$) | 1.60 (6 H, s), 7.19 (1 H, dd, *J*=7.5, 2.0 Hz), 7.52 (1 H, td, *J*=7.5, 1.5 Hz), 7.58 (1 H, td, *J*=7.5, 2.0 Hz), 7.69 (1 H, dd, *J*=7.5, 1.5 Hz) | 148.8, 131.2, 131.1, 129.7, 126.6, 117.0 (Ph), 89.1 (*C*Me$_2$), 28.5 (Me$_2$) | 308 ($M^+$-Me) |

[a] Satisfactory microanalyses (within ±0.3% for C, H, N, and I) and/or high resolution mass spectral data (within ±2 mmu) were obtained for all these compounds. [b] Nmr data were obtained in $CDCl_3$-$CD_3CN$ (10:1).
[c] Obtained as **7**•1/2$H_2O$. [d] Nmr data were obtained in DMSO-$d_6$.

Although we could prepare the cyclic iodinane (**8**) having a nitrato ligand[6] by a similar reaction of **1** and $TMSONO_2$[7] in 74% yield, this method was not preferable due to instability of $TMSONO_2$. More convenient and high-yielding preparation of **8** was attained by the ligand exchange reaction of the known chloro compound (**9**) with 3 eq. of $AgNO_3$ without any catalyst in 98% yield (Table 1).[8] It should be emphasized that the prepared iodinanes (**4**-**8**) are stable at room temperature in the air without any decomposition for more than a week.

The stereostructures of **7** and **8** were determined by their single-crystal X-ray analyses.[9] As shown in Figures 1 and 2, they are approximately T-shaped around the iodine atom similar to those of the reported cyclic iodinanes.[4] The exocyclic C-I bonds (2.11 and 2.13 Å) of **7** are slightly shorter than the endocyclic I-O bonds (2.218 and 2.221 Å), while the relationship is reversed for **8**, which can be explained based on the differences in the electron negativity of the two couples of ligands.

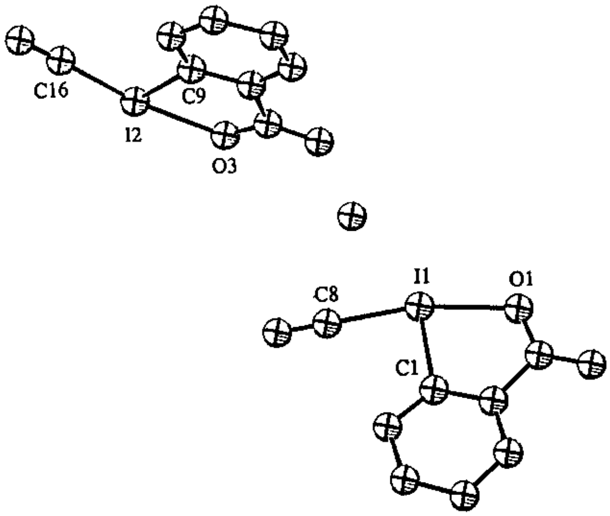


Figure 1 The X-ray crystallographic structure of **7**•1/2$H_2O$. (Two molecules of **7** and one molecule of $H_2O$ are shown.)

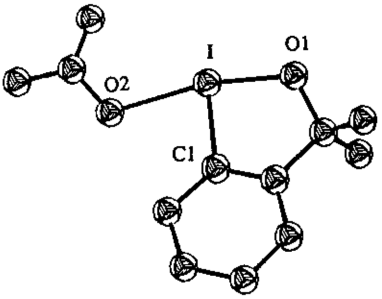


Figure 2 The X-ray crystallographic structure of **8**.

In conclusion, novel cyclic iodinanes having azido, cyano, and nitrato ligands were readily prepared by two types of ligand exchange reactions. The cyclic structures of these compounds enable us to handle them under an aerobic atmosphere. These compounds have potential interest as reagents for the introduction of their ligands, which are currently in progress in our laboratory.

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8. Known compounds (**2**[4a,e] and **9**[4d]) were prepared according to the reported methods. Compound (**3**) was prepared from *o*-iodobenzamide in 67% yield similar to the preparation of **2** and was identical to the authentic sample.[4b] The unknown compound (**1**) was prepared in 97% yield by the ligand exchange reaction of **9** with AgOAc: **1**, mp 126-130 °C ($CH_2Cl_2$-hexane); ir (KBr) $cm^{-1}$: 1638 (CO); $^1H$ nmr ($CDCl_3$) $\delta$: 1.53 (6 H, s), 2.11 (3 H, s), 7.18 (1 H, d, $J$ = 7.5 Hz), 7.44-7.51 (2 H, m), 7.80 (1 H, d, $J$ = 7.5 Hz); $^{13}C$ nmr ($CDCl_3$) $\delta$: 177.2 (CO), 149.3, 130.4, 129.9, 129.8, 126.1, 115.6 (Ph), 84.5 ($CMe_2$), 29.1 ($Me_2$), 21.4 ($MeCO_2$); EI mass *m/z*: 305 ($M^+$-Me).
9. Selected bond distances (Å) and angles (deg) for **7** and **8** are as follows: **7**, C1-I1 2.13(1), O1-I1 2.218(9), I1-C8 2.11(1), C9-I2 2.11(1), O3-I2 2.221(9), I2-C16 2.13(2), C8-I1-C1 89.4(5), C8-I1-O1 166.6(5), C1-I1-O1 77.2(4), C9-I2-C16 88.8(5), C9-I2-O3 77.0(4), C16-I2-O3 165.8(5); **8**, C1-I 2.08(2), O1-I 2.00(2), I-O2 2.26(2), O1-I-C1 81.9(8), O1-I-O2 165.9(8), C1-I-O2 84.1(7).

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