J. Am. Chem. Soc. **2001,** *123,* 1507−1508

Synthesis, Structure, and Reactions of a Tricoordinate 1,2-Iodoxetane

Takayuki Kawashima,* Kazuhisa Hoshiba, and Naokazu Kano

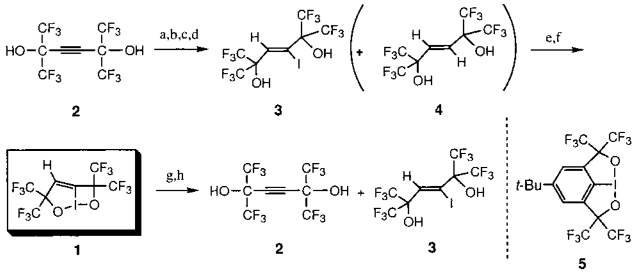
Department of Chemistry
Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received September 15, 2000

Hypervalent iodine compounds have attracted much attention, because of their unique structures and reactivities.[1] For example, Dess−Martin reagent is well-known as a useful oxidizing reagent in organic synthesis.[2] In the course of our study on heteracyclobutanes containing highly coordinate main group elements at the position adjacent to the heteroatom, we have reported oxetanes bearing pentacoordinate group 14 and 15 elements (Si, Ge, Sn, and P) and tetracoordinate group 16 elements (S, Se).[3] Group 14 and 15 analogues underwent the Wittig type reaction to give the corresponding olefins upon heating, whereas some of group 16 element analogues gave the corresponding oxiranes with retention of configuration.[4] It is very interesting that these four-membered ring compounds containing sulfur or selenium, which are considered as formal [2 + 2]-cycloadducts of sulfur or selenium ylides with carbonyl compounds, gave the oxiranes, that is, Corey−Chaykovsky reaction products.[5] Recently, Ochiai and co-workers reported that the reactions of an iodonium ylide with aldehydes afford the corresponding oxiranes.[6] These results prompted us to investigate an oxetane having tricoordinate iodine, that is, a group 17 element analogue. In this paper, we wish to report the synthesis, structure, and reactions of tricoordinate 1,2-iodoxetane **1**, formal [2 + 2]-adduct of an iodonium ylide with a carbonyl compound, using a novel ligand which has been designed.[7]

Sequential treatment of 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-3-hexyne-2,5-diol (**2**)[8] with NaH, $LiAlH_4 - 2NaOMe$,[9] ICl, and aqueous $Na_2S_2O_3$ afforded (*Z*)-1,1,1,6,6,6-hexafluoro-3-iodo-2,5-bis(trifluoromethyl)-3-hexene-2,5-diol (**3**) and 3-hexene-2,5-diol **4** as an inseparable mixture. Treatment of the mixture (1:0.12) of **3** and **4** with neat *t*-BuOCl gave tricoordinate **1** (40% based on disodium salt of **2**) as yellow crystals (Scheme 1).[10]

Scheme 1[a]



[a] (a) 2 molar equivalent NaH, Et_2O, 0 °C → 25 °C; (b) $LiAlH_4$-2NaOMe, Et_2O, 0 °C; reflux, 3 h; (c) ICl, Et_2O, −78 °C; reflux 1 h; (d) aqueous $Na_2S_2O_3$; (e) *t*-BuOCl (neat), 25 °C, 11 h; (f) sublimation, 0.05 mmHg, 100 °C; (g) sealed tube, CD_3CN, 170 °C, 14 h; (h) H_2O.

Two singlets at δ_F −77.3 and −76.8 and singlet at δ_H 8.35 were observed in the ^{19}F and ^1H NMR spectra (acetone-d_6), respectively. In the ^{13}C NMR spectrum, the signal due to the sp^2 carbon adjacent to the iodine shifted downfield (from **3** (δ_C 98.20) to **1** (δ_C 145.65) ($CDCl_3$)), which is a typical feature for an equatorial ligand attached to positively charged central atom of hypervalent species.[4] Although equivalency of geminal trifluoromethyl groups and the above-mentioned downfield shift are consistent with a T-shape structure, the structure was finally determined by X-ray crystallographic analysis.

X-ray analysis showed that it has a distorted T-shape geometry around the central iodine atom (Figure 1A).[11] There have been reported several examples for iodanes containing two oxygen and one carbon atoms.[1,12] Among them, compound **5** bearing two rings, which was reported by Martin and co-workers,[13] was selected for structural comparison of **1**, because of their structural similarity. The intermolecular distance between the iodine and the oxygen of the four-membered ring is 2.821(3) Å, which is much shorter than the sum of van der Waals radii (3.55 Å), indicating a dimeric structure of **1** as same as **5**[13] (Figure 1B). Apical bond angles O−I−O of **1** and **5** are 144.5(1)° and 158.2(2)°, respectively, indicating that the deviation (35.5°) of bond angle O−I−O of **1** from 180° is larger than that (21.8°) of **5**. The apical bond length (2.142(3) Å) of the four-membered ring is longer than that (2.070(3) Å) of the five-membered ring. These results are responsible to the ring strain of the four-membered

---

[1] (a) Zhdankin, V. V.; Stang, P. J. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley−VCH: New York, 1999; Chapter 11, pp 327−358. (b) Ochiai, M. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley−VCH: New York, 1999: Chapter 12, pp 359−387. (c) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123−1178. (d) Koser, G. F. In *The Chemistry of Halides, Pseudo-Halides and Azides, Suppl. D2*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1995; Chapter 21, pp 1173−1274. (e) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431−447.

[2] Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277−7287: Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

[3] Kawashima, T.; Okazaki, R. *Synlett* **1996**, 600−608; Kawashima, T.; Okazaki, R. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press Inc.: Stamford, 1999; Vol. 7, pp 1−41.

[4] Kawashima, T.; Ohno, F.; Okazaki, R.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 12455−12456; Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671−1672.

[5] For the Corey−Chaykovsky reactions, see: Johnson, A. W.; LaCount, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 417−423; Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 3782−3783; Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353−1364; Aubé, J. In *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 822−825. For the related reactions of aminosulfoxonium ylides, see: Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341−347.

[6] Ochiai, M.; Kitagawa, Y.; Yamamoto, S. *J. Am. Chem. Soc.* **1997**, *119*, 11598−11604.

[7] Phosphoranes bearing a similar tridentate ligand were synthesized by the reaction of arylethynylphosphines with 2 mol equiv of hexafluoroacetone, see: Aly, H. A. E.; Barlow, J. H.; Russell, D. R.; Smith, D. J. H.; Swindles, M.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1976**, 449−450; Huang, Y.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800−7802; Huang, Y.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1993**, *115*, 4031−4039; Huang, Y.; Bentrude, W. G. *J. Am. Chem. Soc.* **1995**, *117*, 12390−12396; Huang, Y.; Arif, A. M.; Bentrude, W. G. *Phosphorus, Sulfur, Silicon* **1995**, *103*, 225−233.

[8] Morken, P. A.; Burton, D. J. *Synthesis* **1994**, 969−972.

[9] Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245−4247.

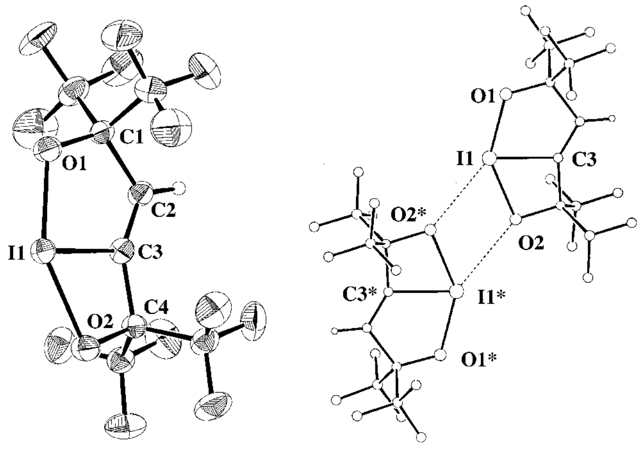
[10] **1**: yellow crystal; mp 121−127 °C (decomp.); ^1H NMR (270 MHz, acetone-d_6) δ 8.35 (s); $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$) δ 115.15 (s, $\underline{C}H{=}C{-}I$), 122.22 (q, $^1J_{CF}$ = 288 Hz, $C(\underline{C}F_3)_2$), 122.50 (q, $^1J_{CF}$ = 288 Hz, $C(\underline{C}F_3)_2$), 146.44 (s, $CH{=}\underline{C}$-I). The signals due to $\underline{C}(CF_3)_2$ could not be observed; $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6) δ 84.16 (sept, $^2J_{CF}$ = 33 Hz, $\underline{C}(CF_3)_2$), 96.53 (sept, $^2J_{CF}$ = 31 Hz, $\underline{C}(CF_3)_2$), 117.21 (s, $\underline{C}H{=}C{-}I$), 123.90 (q, $^1J_{CF}$ = 286 Hz, $C(\underline{C}F_3)_2$), 124.05 (q, $^1J_{CF}$ = 287 Hz, $C(\underline{C}F_3)_2$), 145.65 (s, $CH{=}\underline{C}$-I); ^{19}F NMR (254 MHz, acetone-d_6) δ −77.3 (s, $C(C\underline{F}_3)_2$), −76.8 (s, $C(C\underline{F}_3)_2$); Anal. Calcd for $C_8HO_2F_{12}I$: C, 19.85; H, 0.21; I, 26.22: Found: C, 19.55; H, 0.34; I, 25.87; GC−MS *m*/*z* 415 ($M^+ - CF_3$).

[11] **1**: $C_8HF_{12}O_2I$, FW = 483.98, crystal dimensions (mm) 0.30 × 0.15 × 0.15, monoclinic, space group $P2_1/c$, a = 6.845(2) Å, b = 17.687(8) Å, c = 10.888(4) Å, β= 98.28(2)°, V = 1304.4(8) Å^3, Z = 4, D_{calcd} = 2.464 g/cm^3, R_1= 0.049, (wR_2= 0.075). Full details of the crystallographic structure analysis are described in the Supporting Information available.

[12] Etter, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5326−5331; Ochiai, M.; Ito, T.; Masaki, Y.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 6269−6270; Ochiai, M. Ito, T.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1993**, 218−219; Akai, S.; Okuno, T.; Egi, M.; Takada, T.; Tohma, H.; Kita, Y. *Heterocycles* **1996**, *42*, 47−51.

[13] (a) Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 1024−1027. (b) Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3803−3811.

10.1021/ja003393a CCC: $20.00



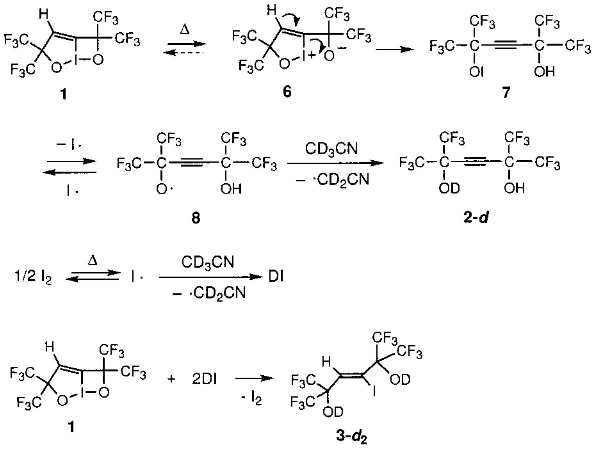
(A) (B)

Figure 1. (A) ORTEP drawing of **1** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): I1−O1, 2.070(3); I1−O2, 2.142(3); I1−C3, 2.075(4); O2−C4, 1.401(5); C3−C4, 1.519(6); O1−I1−O2, 144.5(1); O1−I1−C3, 79.3 (1); I1−C3−C4, 95.8(3); C3−C4−O2, 102.2(3); C4−O2−I1, 96.7(2); O2−I1−C3, 65.2(1); O1−I1−C3−C2, 2.5(4); I1−C3−C4−O2, 0.0(3). (B) Intermolecular interaction. Intermolecular distance (Å): I1−O2*, I1*−O2, 2.821(3).

ring. Additionally, the intermolecular interaction of the apical oxygen with the iodine plays an important role in elongation of the apical bond like **5**.[14] The four-membered ring is almost planar, judging from the torsion angle I(1)−C(3)−C(4)−O(2) (0.0(3)°) and the sum of bond angles of the four-membered ring (359.9°), which is a typical feature of most of oxetanes bearing highly coordinate main group elements.[3] This is the first example of a tricoordinate 1,2-iodoxetane.

Thermolysis of **1** (sealed tube, CD_3CN) gave almost quantitatively **2** together with a trace of **3**.[15] Plausible formation mechanism of **2** and **3** is as follows: heterolysis of the I−O bond takes place to give intramolecular iodonium oxide **6**, which undergoes intramolecular or intermolecular deprotonation with elimination of I−O group to give hypoiodite **7** because of high leaving ability of iodonio groups as demonstrated by Stang et al. and Ochiai et al.[1b,16] Homolytic cleavage of I−O bond of **7** gives the alkoxy radical **8** and I•, the former of which abstracts deuterium from CD_3CN to give **2**-d_1. On the other hand, iodo radical dimerizes to iodine, and some iodo radical, which equilibrates with iodine, abstracts deuterium from CD_3CN to afford DI, although this step seems to be very endothermic. The reaction of unreacted **1** with DI gives **3**-d_2 and I_2, which is evidenced by a separate experiment. All deuterioxy groups can be converted to hydroxy groups by water (Scheme 2). Oxidizing capacity of **1** was also demonstrated by the reaction with benzyl alcohol giving benzaldehyde (48%) together with (*Z*)-**3**.

Scheme 2. Plausible Mechanism



In summary, we have succeeded in the synthesis of tricoordinate 1,2-iodoxetane, a formal [2 + 2]-adduct of an iodonium ylide and a carbonyl compound. However, no information on the expected thermal reactivity, that is, olefin or oxirane formation, was obtained, because the competitive reaction took place. Further investigations including replacement of hydrogen of the methine group by an appropriate substituent such as phenyl group are now in progress.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (A) No. 12304037 (T.K.) from the Ministry of Education, Science, Sports and Culture, Japan. We thank Central Glass and Toso Akzo Co. Ltd. for the gifts of organofluorine compounds and alkyllithiums, respectively.

Supporting Information Available: An experimental procedure for the synthesis of **1** (PDF) and X-ray crystallographic data with tables of thermal and positional parameters, bond lengths, and bond angles for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003393A

---

(14) The apical bond (2.113(3) Å) with intermolecular interaction is slightly longer than another apical bond (2.077 (3) Å), see ref 13b.

(15) In some run, an unidentified product was also obtained besides **2** and **3**.

(16) For iodonio groups as a hyperleaving group, see: Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360−3367; For a similar *anti*-*β*-elimination from (*Z*)-1-decenyl(phenyl)iodonium perchlorate, see: Okuyama, T.; Takino, T.; Sato, K.; Oshima, K.; Imamura, S.; Yamataka, H.; Asano, T.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 243−257. For intramolecular *syn*-*β*-elimination from (*E*)-*β*-alkylvinyl-(phenyl)-iodonium salts, see: Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059−7061; Okuyama, T.; Takino, T.; Sato, K.; Ochiai, M. *J. Am. Chem. Soc.* **1998**, *120*, 2275−2282.