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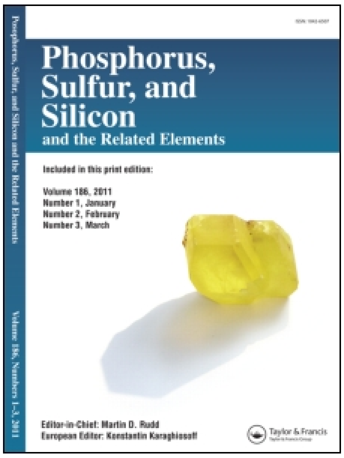

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Synthesis and Structure of a Tricoordinate 1,2-Iodoxetane

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Synthesis and Structure of a Tricoordinate 1,2-Iodoxetane

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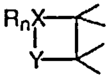
The title compound was successfully synthesized as yellow crystals by oxidative cyclization of the corresponding 3-iodo-3-hexene-2,5-diol with *t*-BuOCl. The NMR spectral data was consistent with a T-shape structure, which was confirmed by X-ray crystallographic analysis. Strong intermolecular interaction between the iodine atom and the oxygen atom of the four-membered ring was observed in the solid state.

Keywords: tricoordinate; 1,2-iodoxetane; T-shape structure; X-ray crystallographic analysis; oxidative cyclization

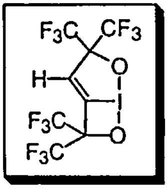
INTRODUCTION

In the course of our study on heteracyclobutanes **1** bearing highly coordinate main group elements at the position adjacent to the heteroatom we have reported that oxetanes containing pentacoordinate group 14 and 15 elements undergo the Wittig type reaction to yield the corresponding olefins upon heating, whereas some of group 16 element analogues give the corresponding oxiranes with retention of configuration.[1,2] Recently, Ochiai and coworkers reported that the reactions of an iodonium ylide with aldehydes afford the corresponding oxiranes.[3] These results prompted us to investigate a group 17 element analogue. In this paper, we wish to report the synthesis and structure of tricoordinate 1,2-iodoxetane **2**, formal [2+2]-adduct of an iodonium ylide with a carbonyl compound.



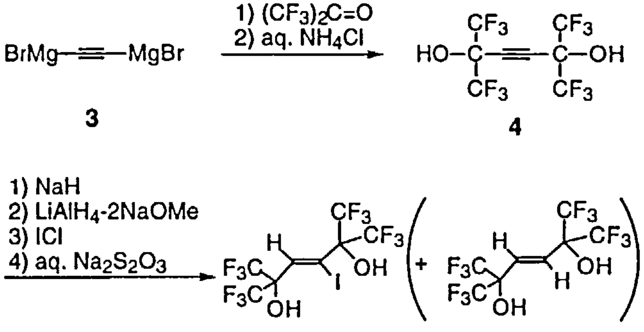
1

X= P, Si^-, Ge^-, Sn^-,
S, Se
Y= O, NPh

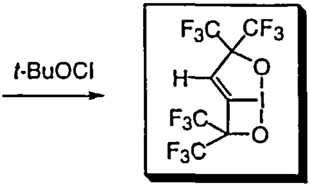


2

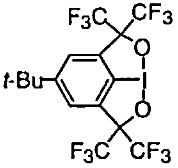
RESULTS AND DISCUSSION



3 **4** **5** **6**



2



7

The reaction of di-Grignard reagent **3** with hexafluoroacetone gave the corresponding 3-hexyne-2,5-diol **4** according to the literature.[4]

Sequential treatment of **4** with NaH, $LiAlH_4$-2NaOMe,[5] 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 (**5**) and (*E*)-3-hexene-2,5-diol **6** as inseparable mixture (1:0.12). Treatment of a mixture of **5** and **6** with neat *t*-BuOCl gave tricoordinate 1,2-iodoxetane **2** as yellow crystals.[6]

Two singlets at δ_F −77.3 and −76.8 and singlet at δ_H 7.52 were observed in the ^{19}F and ^1H NMR spectra, respectively. In the ^{13}C NMR spectrum, ca. 48 ppm downfield-shift was observed for the signal due to the sp2 carbon adjacent to the iodine, which is a typical feature for an equatorial ligand attached to positively charged central atom of hypervalent species.[2] Although equivalency of geminal trifluoromethyl groups and the above-mentioned downfield shift were consistent with a T-shape structure, the structure was finally determined by X-ray crystallographic analysis.

The X-ray analysis showed that it has a distorted T-shape geometry around the central iodine atom. Apical bond angle O-I-O (144.5(1)°) of **2** is smaller than that (158.2(2)°) of **7**, which was reported by Martin et al.[7] 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 ring. The four-membered ring is almost planar, judging from the torsion angle I(1)-C(3)-C(4)-O(2) (0.0(3)°), which is a typical feature of most of oxetanes bearing highly coordinate main group elements.[1,2] Interestingly, there is strong interaction between the iodine atom and the oxygen atom of the four-membered ring, so that **2** has a dimeric structure like **7**. This is the first example of a tricoordinate 1,2-iodoxetane.

Further investigations including the thermolysis are in progress.

ACKNOWLEDGEMENTS

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[6] **2**: yellow crystal; mp 121–127 °C (decomp.); ^{1}H NMR (270 MHz, acetone-d_6) δ8.35 (s); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 84.2 (sept, $^{2}J_{CF}$= 29 Hz, $\underline{C}(CF_3)_2$), 96.5 (sept, $^{2}J_{CF}$= 31 Hz, $\underline{C}(CF_3)_2$), 117.2 (s, $\underline{C}$H=C-I), 123.9 (q, $^{1}J_{CF}$ = 286 Hz, $C(\underline{C}F_3)_2$), 124.0 (q, $^{1}J_{CF}$ = 287 Hz, $C(\underline{C}F_3)_2$), 145.6 (s, CH=$\underline{C}$-I); ^{19}F NMR (254 MHz, acetone-d_6) δ −77.3 (s, $C(\underline{C}F_3)_2$), −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).

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