Synthesis of Cyclic Iodonium Ylides—$3H$-1λ^3-Benziodol-1-ylium Ylides *via* Transylidation of Iodonium Ylides to Iodides

Rui-Yang Yang,[a] Li-Xin Dai*[a] and Cheng-Gang Chen[b]

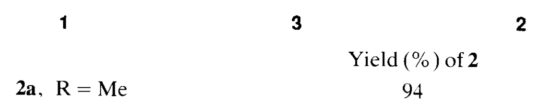
[a] *Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China*

[b] *Central Laboratory, Hangzhou University, Hangzhou, 310028, China*

Cyclic iodonium ylides are synthesised *via* an unprecedented transylidation of iodonium ylide to aryl iodides; the structure of one cyclic iodonium ylide is determined by X-ray crystallography.

Hypervalent iodonium ylides are of great interest in organic chemistry.[1] Since the discovery of the first stable iodonium ylide, which was synthesised *via* reaction of 5,5-dimethylcyclohexane-1,3-dione with (difluoroiodo)benzene $C_6H_5IF_2$,[2] a great number of stable iodonium ylides have appeared,[3] and many synthetic applications with them have also emerged.[4] However, although cyclic hypervalent iodonium compounds are very important both theoretically and synthetically,[5] cyclic iodonium ylides have never been prepared since they cannot be synthesised by a usual method. In this communication, we report the synthesis, structure and chemistry of a new series of stable iodonium ylides **2a-g** in which the iodine atoms and the neighbouring carbanions are ring members of the iodonioindene cycles.

Cyclic iodonium ylides **2a–g** were synthesised by an intramolecular transylidation of a preformed acyclic iodonium ylide (Scheme 1). The preformed acyclic iodonium ylide **3** was heated in benzene in the presence of a catalytic amount of $Cu(acac)_2$ (Hacac = pentane-2,4-dione) and transformed to cyclic ylide **2** in good to excellent yield.† Although the transylidation reactions of iodonium ylides with nucleophilic heteroatom species, such as S, N, P and As, appear fairly general, the transylidation of an iodonium ylide to another iodine atom of aryl iodides is unprecedented. This transylidation reaction probably involves dissociation of the ylide **3** into iodobenzene and dicarbonylcarbene,[6] the newly formed carbene was then trapped immediately by the intramolecular iodine atom to form ylide **2**.



1 **3** **2**

	Yield (%) of **2**
2a, R = Me	94
b, R = *p*-$MeOC_6H_4$	80
c, R = Ph	87
d, R = *p*-ClC_6H_4	61
e, R = *p*-MeC_6H_4	92
f, R = *p*-$C_6H_5OC_6H_4$	80
g, R = α-$C_{10}H_7$	28

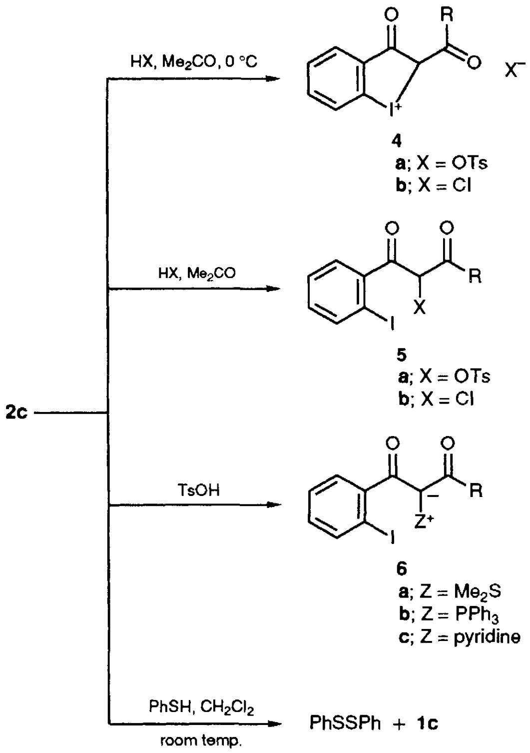
Scheme 1 *Reagents and conditions*: i, $PhI(OAc)_2$, KOH, MeOH, 0 °C; ii, benzene, reflux, $Cu(acac)_2$, 1 h

A single crystal of **2a** was obtained from methanol. The ORTEP drawing of **2a** is depicted in Fig. 1.‡ An interesting

---

† *Selected data*: compound: IR ν_{max}/cm^{-1}; ^1H NMR ([$^2H_6$]dimethyl sulfoxide)/δ; m.p./°C. For **2a**: 1575, 1520; 2.72 (s, 3 H), 7.80–8.14 (m, 4 H); 173–175. For **2b**: 1575, 1535; 3.86 (s, 3 H), 6.98–8.52 (m, 8 H); 147–148. For **2c**: 1575, 1540; 7.42–8.32 (m, 9 H); 161.5–162.5. For **2d**: 1570, 1530; 7.52–8.36 (m, 8 H); 164–165. For **2e**: 1575, 1540; 2.40 (s, 3 H), 7.27–8.30 (m, 8 H); 159.5–160.5. For **2f**: 1585, 1540; 7.00–8.56 (m, 13 H); 159–160. For **2g**: 1570, 1545; 7.40–8.46 (m, 11 H); 151–153. All new compounds gave satisfactory elemental analyses.

‡ *Crystal data* for **2a**: monoclinic, $P2_1/c$, M_r = 287.08, a = 14.795(2), b = 5.361(2), c = 12.981(4) Å; β = 119.33(4)°, V = 897.6(3) Å^3, Z = 4, $F(000)$ = 548, D_c = 2.12 g cm^{-3}, μ(Mo-Kα) = 34.9 cm^{-1}, λ(Mo-Kα) = 0.70930 Å. Crystal size: 0.08 × 0.08 × 0.30 mm. Data were collected on Enraf-Nonius CAD4 Diffractometer. 1763 reflections with $F > 3\sigma(F)$ and 2θ up to 52 were used in the refinement. Final R factors: R = 0.029 and R_w = 0.033. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

feature of the solid-state structure of **2a** is the near planarity of the whole molecule. All the C, I and O atoms are essentially coplanar, the largest deviation from the best least-squares plane fitted to them is 0.062 Å. This feature arises from the secondary bonding interaction between the *exo*-carbonyl oxygen O(2) and I. They are in *cis* configuration and the distance I–O(2) is 2.898 Å. The I–C(8)–C(9) angle is more acute (110.5°) than the expected 120°. Moreover, the bond distances of C(7)–O(1) and C(9)–O(2) are 1.25 and 1.24 Å, respectively, they are slightly longer than the normal expected value of a C–O double bond.[7] The C(7)–C(8) and C(8)–C(9) distances of 1.41 Å are slightly shorter than the normal C–C single bond (1.46 Å).[8] These indicate that the negative charge, formally located on C(8), has delocalized to some extent towards the carbonyl oxygen atoms. This agrees well with the spectral evidence of the abnormal IR stretching frequency of the carbonyl groups (ν/cm^{-1} 1535 and 1575) in **2a–g**. The bond distance I–C(8) (2.084 Å) is in accordance with the value of an iodonium ylide. Although the C(1)–I–C(8) bond angle (82.1°) is smaller than the usual one, the small C–X–C angle is characteristic of a halonium ylide structure. In addition to the intramolecular I–O(2) interaction, the distance between I and O(1) of the nearest neighbouring molecule is only 2.892 Å, the same magnitude as the intramolecular I–O(2) distance. This value is significantly less than the sum of the van der Waals radii (3.5 Å) of I–O.[9] Thus, the ylides form a secondary bonded polymer extending along the *c* direction in the crystal.

The cyclic iodonium ylides **2a–g** are much more stable than their acyclic analogues **3a–g**. In contrast to the instability of the acyclic iodonium ylides **3a–g**, the crystalline cyclic ylides are stable on storing at room temperature for more than four months without any change in appearance and ^{1}H NMR spectra. The reactions depicted in Scheme 2 demonstrate the ylidic nature of **2a–g**. When **2c** was reacted with HCl or p-MeC$_6$H$_4$SO$_3$H(TsOH) in acetone at 0 °C, the novel cyclic iodonium salt **4** was obtained in good yield. On extension of the reaction time or raising of the reaction temperature, **4** could be further converted into **5**. The transylidation of acyclic iodonium ylides with nucleophilic heteroatom species (S, P, N) occurs smoothly either by the use of light or a copper catalyst, while **2c** is rather stable under these conditions. However, the transylidation of **2c** took place in the presence of a catalytic amount of TsOH and the sulfonium, phosphonium and ammonium ylides were isolated in 68, 52 and 87% yields, respectively. The oxidizing property of **2c** is exemplified by the reaction with thiophenol to afford diphenyl disulfide and **1c**. The chemical reactions of **2c** resemble the typical properties of an iodonium ylide.

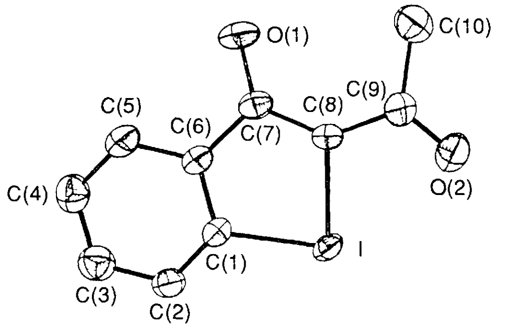


Fig. 1 ORTEP view of ylide **2a**, H atoms are omitted for clarity

We thank the Chinese Academy of Sciences and National Natural Science Foundation of China for financial support.

Received, 13th July 1992; Com. 2/03718A

References

1 For an excellent review, see: G. F. Koser, in *The Chemistry of Functional Groups, Supplement D*, ed. S. Patai, Wiley, New York, 1993, ch. 18, pp. 774–806.
2 E. Gudrinietse, O. Neilands and G. Vanag, *J. Gen. Chem. USSR (Engl. Transl.)*, 1957, **27**, 2777.
3 R. M. Moriarty, I. Prakash, O. Prakash and W. A. Freeman, *J. Am. Chem. Soc.*, 1984, **106**, 6082 and references cited therein; L. Hadjiarapoglou, S. Spyroudis and A. Varvoglis, *J. Am. Chem. Soc.*, 1985, **107**, 7178; S. Zhu and Q. Chen, *J. Chem. Soc., Chem. Commun.*, 1990, 1459; J. Hackenberg and M. Hanack, *J. Chem. Soc., Chem. Commun.*, 1991, 470; A. G. Arduengo, M. Kline, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1991, **113**, 9704.
4 R. M. Moriarty and R. K. Vaid, *Synthesis*, 1990, 431; R. M. Moriarty, O. Prakash, R. K. Vaid and L. Zhao, *J. Am. Chem. Soc.*, 1989, **111**, 6443; S. Kalogiannis and S. Spyroudis, *J. Org. Chem.*, 1990, **55**, 5041.
5 A. Varvoglis, *Chem. Soc. Rev.*, 1981, **10**, 377; T. T. Nguyen and J. C. Martin, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 1, pp. 563.
6 Y. Hayasi, T. Okada and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2506; J. N. C. Hood, D. Lloyd, W. A. MacDonald and T. M. Shepherd, *Tetrahedron*, 1982, **38**, 3355.
7 G. Berthier and J. Serre, *The Chemistry of the Carbonyl Group*, ed. S. Patai, Wiley, New York, 1966, ch. 1, pp. 1–78.
8 F. S. Stephens, *J. Chem. Soc.*, 1965, 5640.
9 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.