ELSEVIER

Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1993, **3(3)**, 81–82

Mendeleev
Communications

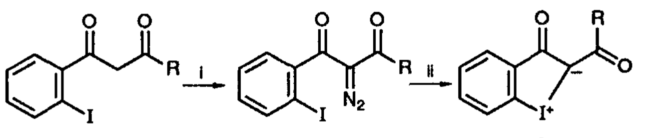
A New Route to Cyclic Iodonium Ylides—3*H*-1^3-Benziodol-1-ylium Ylides *via* Intramolecular Capture of Rhodium-Generated -Dicarbonyl Carbenes by Aryl Iodides

Rui-Yang Yang and Li-Xin Dai*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
345 Lingling Lu, Shanghai, 200032, China. Fax +86 21 433 5712

A new method for the synthesis of cyclic iodonium ylides *via* $Rh_2(OAc)_4$ catalysed decomposition of α-diazo-β-dicarbonyl compounds is described.

Hypervalent iodonium ylides have received much attention in recent years[1] due to their synthetic versatility in organic synthesis as well as their theoretical interest.[2,3] They are generally synthesised by reaction of hypervalent iodine reagents with active methylene compounds.[1,3] However, there are still a few methods other than this: the thermal decomposition of dicyanodiazoimidazole in aryl halides leads to the corresponding halonium ylides;[4] refluxing of iodosobenzene with electron-deficient acetylenes gave iodonium ylide;[5] and the rhodium-catalysed decomposition of 2-diazocyclohexane-1,3-dione in aryl iodides provided the iodonium ylides of cyclohexane-1,3-diones.[6] Very recently, it was found that nucleophilic carbene could also be trapped by pentafluoroiodobenzene to give an unusual reversed iodonium



1 2 3

		Yield(%) of 3
3a	R = Me	95
3b	R = *p*-MeOC$_6$H$_4$	89
3c	R = Ph	84
3d	R = *p*-ClC$_6$H$_4$	81
3e	R = *p*-MeC$_6$H$_4$	85
3f	R = *p*-C$_6$H$_5$OC$_6$H$_4$	82
3g	R = α-C$_{10}$H$_7$	41

Scheme 1 *Reagents and conditions*: i, TsN$_3$, NEt$_3$, CH$_2$Cl$_2$; ii, Rh$_2$(OAc)$_4$ (cat.), benzene, 50 °C, 1 h.

ylide.[7] Because of the instability of iodonium ylides, these four methods are not general, they are only limited to the synthesis of iodonium ylides with specific structural entities. As part of our studies in hypervalent iodonium ylides,[8,9] we recently reported an unprecedented transylidation reaction of iodonium ylides to iodides which gave the first synthesis of cyclic iodonium ylides—3*H*-1λ^3-benziodol-1-ylium ylides.[8] We presume that the transylidation reaction might involve carbene intermediates. If this is true, it should be possible to synthesise the cyclic iodonium ylide *via* Rh$_2$(OAc)$_4$ decomposition of α-diazo-β-dicarbonyl compounds **2**, which is proposed to take place *via* an intermediate carbene mechanism.[6] We therefore studied the intramolecular capture of Rh$_2$(OAc)$_4$-generated β-dicarbonyl carbenes by aryl iodides.

The diazo compounds **2** (1 mmol) were dissolved in benzene (3 ml), 5 mg of Rh$_2$(OAc)$_4$ was added and the reaction system was stirred at 50 °C for 1 h. Within 10 min, the yellow cyclic iodonium ylides **3** began to precipitate from the solution. Except when R = α-naphthyl, all R substituents gave very high yields of **3**. The yields are comparable to those of the iodine to iodine transylidation reaction of acyclic iodonium ylides to aryl iodides,[8] and strengthen our assumptions about the mechanism of the transylidation. When R = α-naphthyl, there might be competition between the intramolecular aryl iodide capture of carbene and the intramolecular C–H bond insertion; thus, the yield of **3g** is much lower than that of other R substituents. The cyclic iodonium ylides **3** with I$^+$ and C$^-$ as members of the cycles behave the same in every respect as those obtained by the iodine to iodine transylidation process.[8]

In conclusion, a new method for the synthesis of cyclic iodonium ylides has been developed *via* Rh$_2$(OAc)$_4$-catalysed decomposition of α-diazo-β-dicarbonyl compounds and intramolecular capture of carbenes by aryl iodides. The results strengthen our postulation about the mechanism of intramolecular transylidation reactions of iodonium ylides to iodides.

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

References

1 For an excellent review, see: G. F. Koser, in *The Chemistry of Functional Groups, Supplement D*, ed. S. Patai, Wiley, New York, 1983, ch. 18, pp. 774–806.
2 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.
3 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.
4 W. A. Sheppard and O. W. Webster, *J.Am.Chem.Soc.*, 1973, **95**, 2695.
5 N. S. Zefirov, S. I. Kozhushkov and V. V. Zhdomkin, *Zh.Org.Khim.*, 1988, **24**, 1560 (*Chem.Abstr.*, 1989, **110**, 192323).
6 R. M. Moriarty, B. R. Bailey, O. Prakash and I. Prakash, *J.Am.Chem.Soc.*, 1985, **107**, 1375.
7 A. J. Arduengo, M. Kline, J. C. Calabrese and F. Davidson, *J.Am.Chem.Soc.*, 1991, **113**, 9704.
8 R.-Y. Yang, L.-X. Dai and C.-G. Chen, *J.Chem.Soc., Chem.Commun.*, 1992, 1487.
9 R.-Y. Yang and L.-X. Dai, *Synthesis*, in the press; R.-Y. Yang, L.-X. Dai and R.-J. Ma, *Hetereoat. Chem.*, in the press.

Received: Cambridge, 13th January 1993
Moscow, 19th January 1993; Com: 3/00215B