

Rhodium(II)-Catalyzed Transylidation of Aryliodonium Ylides: Electronic Effects of Aryl Groups Determine Their Thermodynamic Stabilities

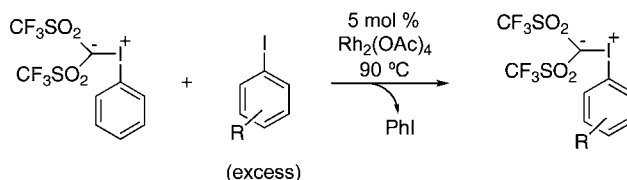
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ABSTRACT

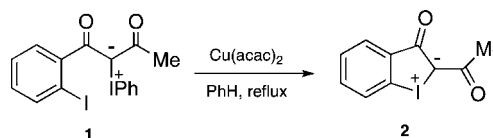


Intermolecular transylidations between aryliodonium ylides under catalytic conditions were developed. Heating a solution of phenyliodonium bis(trifluoromethylsulfonyl)methylide in a large amount (80 equiv) of a substituted iodobenzene in the presence of 5 mol % of rhodium(II) acetate as a catalyst transfers the bis(trifluoromethylsulfonyl)-methylidene group to the iodine(I) atom and affords a substituted aryliodonium ylide in a good yield. Reversible nature of the catalytic intermolecular transylidation makes it possible to evaluate the thermodynamic stability of aryliodonium ylides.

Because of the hyper-leaving group ability of aryl- λ^3 -iodanyl groups,¹ aryliodonium ylides serve as excellent progenitors for generation of singlet carbenes (or carbenoids) under thermal conditions² and transfer the alkylidene groups to heteroatom nucleophiles such as nitrogen heterocycles and sulfides.^{3,4} Use of copper(I) and (II) catalysts or photochemical irradiation accelerates the transylidation with nucleophiles, providing a useful preparative method for pyridinium, phosphonium, sulfonium, sulfoxonium, and arsonium ylides, etc.^{5,6}

In 1992, Dai and co-workers reported the first example of transylidations between aryliodonium ylides under copper-catalyzed conditions; the alkylidene group of aryliodonium ylide **1** was transferred in an intramolecular fashion to the close-neighboring iodine(I) atom attached to the aromatic moiety via the formation of active Cu-carbenoid species, yielding the cyclic iodonium ylide **2** (Scheme 1).⁷ In spite

Scheme 1



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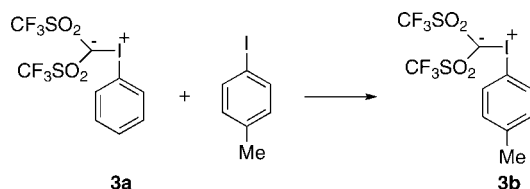
of the surging interest and activity in the ylide chemistry, the intermolecular version of transylidation between aryliodonium ylides remains unknown.⁸ In the reaction of phenyliodonium bis(phenylsulfonyl)methylide with methyl

and primary alkyl iodides (EtI and *n*-BuI), which affords C–I insertion products, the intermediacy of labile alkyl-iodonium ylides produced via transylidation has been proposed but the alkyl-iodonium ylides were neither detected nor isolated.^{9,10}

We report herein the first example of well-characterized intermolecular transylidations between aryliodonium ylides **3** under rhodium(II)-catalyzed conditions. The transylidation reaction makes it possible to evaluate the thermodynamic stability of aryliodonium ylides **3** with a wide range of substituents at the *para* position.

Attempted thermal decomposition of phenyliodonium bis(trifluoromethylsulfonyl)methylide (**3a**)⁶ in a large excess (80 equiv) of *p*-iodotoluene at 90 °C for 5 h showed no evidence for thermal transylidation reactions and the ylide **3a** was recovered unchanged. Heating at 170 °C for 2 h resulted in the partial transfer of bis(trifluoromethylsulfonyl)methylidene group to the iodine(I) atom, yielding *p*-tolyliodonium ylide **3b**, albeit in a very low yield. Prolonged heating at that temperature resulted in the extensive decomposition of **3a** (Table 1, entries 1–3).

Table 1. Transylidation of Iodonium Ylide **3a** to *p*-Iodotoluene^a



entry	additive ^b	temp (°C)	<i>t</i> (h)	yield (%) ^c
1	–	90	5	– (94)
2	–	170	2	7 (80)
3	–	170	24	– (4)
4	CuCl	90	5	38 (38)
5	CuI	90	5	14 (50)
6	CuCN	90	5	11 (85)
7	Cu(acac) ₂	90	5	33 (38)
8	Rh ₂ (OAc) ₄	90	5	97 (3)

^a Reaction conditions: *p*-iodotoluene (80 equiv)/Ar. ^b 5 mol %. ^c Isolated yields. Parentheses are yields of recovered ylide **3a**.

Use of a small amount (5 mol %) of traditional copper catalysts such as CuCl and Cu(acac)₂ lowered the transyl-

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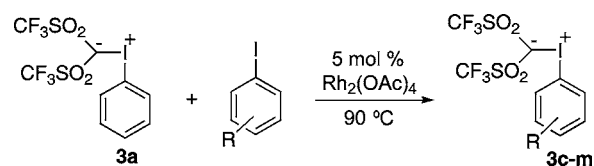
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(8) Recently, we reported the intermolecular transfer of the alkylidene groups of arylbromonium ylides to aryl halides (iodides, bromides, and chlorides) yielding a variety of aryliodonium, bromonium, and chloronium ylides under thermal or metal-catalyzed conditions. See: Ochiai, M.; Tada, N.; Okada, T.; Sota, A.; Miyamoto, K. *J. Am. Chem. Soc.* **2008**, 130, 2118.

idation temperature and afforded modest yields (33–38%) of **3b** at 90 °C for 5 h. CuI and CuCN were less effective. Rhodium(II) acetate was found to be the catalyst of choice for carbenoid capture by *p*-iodotoluene, yielding the iodonium ylide **3b** in 97% yield after purification by preparative TLC using 1:1 hexane-ethyl acetate (Table 1, entry 8). To the best of our knowledge, this is the first successful example of the intermolecular transylidation between aryliodonium ylides.

Rhodium(II) acetate-catalyzed transfer of the bistriflyl-methylidene group to substituted iodobenzenes provides a direct route for the synthesis of a variety of aryliodonium ylides **3** (Table 2). Thus, *p*-methoxy, *o*-methyl, *m*-methyl,

Table 2. Rh(II)-Catalyzed Transylidation of Iodonium Ylide **3a**^a



entry	iodoarene	<i>t</i> (h)	3 yield (%) ^b
1	<i>p</i> -MeOC ₆ H ₄ I	5	3c 84
2	<i>o</i> -MeC ₆ H ₄ I	5	3d 92
3	<i>m</i> -MeC ₆ H ₄ I	5	3e 92
4	3,5-Me ₂ C ₆ H ₃ I	5	3f 82
5	<i>p</i> -FC ₆ H ₄ I	5	3g 89
6	<i>p</i> -ClC ₆ H ₄ I	7	3h 78
7	<i>p</i> -BrC ₆ H ₄ I	10	3i 77
8	<i>p</i> -CF ₃ C ₆ H ₄ I	24	3j 77
9	<i>p</i> -NO ₂ C ₆ H ₄ I ^c	24	3k 38 ^d
10	C ₆ F ₅ I	24	3l – ^d
11	CF ₃ (CF ₂) ₂ CH ₂ I	24	3m –

^a Reaction conditions: an aryl iodide (80 equiv)/Rh₂(OAc)₄ (5 mol %)/90 °C/Ar. ^b Isolated yields. ^c In 1,2-dichloroethane. ^d Recovered ylide **3a**: 49% (entry 9) and 81% (entry 10).

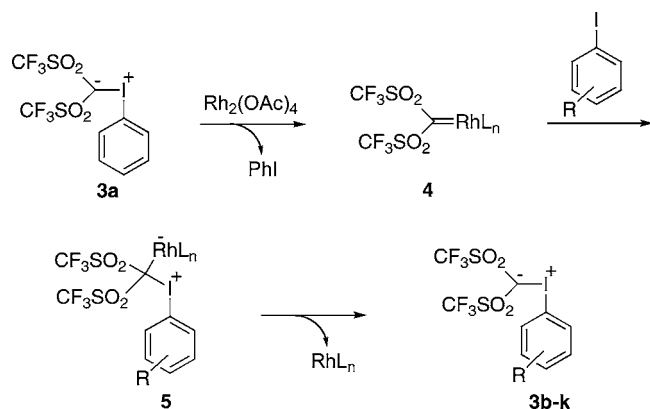
3,5-dimethyl, *p*-fluoro, *p*-chloro, *p*-bromo, and *p*-trifluoromethyl substituted aryliodonium ylides **3c–j** were prepared from the ylide **3a** in the presence of 5 mol % of rhodium(II) acetate at 90 °C in high yields. Use of iodobenzenes with electron-withdrawing substituents (Cl, Br, and CF₃) slows down the rate of transylidation and requires longer reaction times (7–24 h, Table 2, entries 6–8). Carbenoid capture by electron deficient *p*-nitroiodobenzene was carried out in 1,2-dichloroethane solution at 90 °C because of its higher melting point (175–177 °C), and this afforded the ylide **3k** in a modest yield (38%). Pentafluoroiodobenzene and heptafluoroiodobutane showed no evidence for formation of the corresponding iodonium ylides **3l** and **3m**, respectively.

A reaction mechanism involving the formation of a metal–carbenoid complex as an active species is depicted in Scheme

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(10) For transylidations between a diazo compound and a halonium ylide, see: (a) Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, 95, 2695. (b) Janulis, E. P.; Arduengo, A. J. *J. Am. Chem. Soc.* **1983**, 105, 3563. (c) Moriarty, R. M.; Bailey, B. R.; Prakash, O.; Prakash, I. *J. Am. Chem. Soc.* **1985**, 107, 1375.

Scheme 2

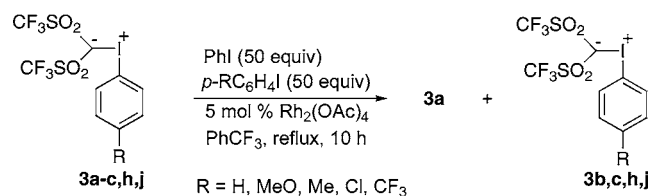


2. Nucleophilic attack of an iodine atom of aryl iodide to rhodium-carbenoid **4**, produced from **3a** via reductive elimination of a phenyl- λ^3 -iodanyl hyper-leaving group,¹ will afford the complex **5**. Regeneration of rhodium(II) catalyst from **5** produces the substituted phenyliodonium ylides **3b-k**.

It has been shown to be difficult to generalize the effects of substituents of the aromatic ring on thermal stability of arylidonium ylides, since the same substituent variation may operate in opposite directions in a different class of iodonium ylides.^{4d,11} Therefore, it seems to be desirable to evaluate the substituent effects on the thermodynamic stability of arylidonium ylides **3** to gain some insight into the intrinsic nature of the ylides. The mechanism of our transylidations, shown in Scheme 2, would expect the reversible nature of the reactions, which makes it possible to assess the thermodynamic stability of iodonium ylides **3**.

Product ratios of the catalyzed transylidations to a mixture of an unsubstituted and a substituted iodobenzene with *p*-MeO, *p*-Me, *p*-Cl, or *p*-CF₃ group were measured in refluxing (trifluoromethyl)benzene as a solvent for 10 h by competitive reactions using ¹H NMR, in which a mixture of a 50-fold excess of iodobenzene and a substituted iodobenzene was used (Table 3). The competitive transylation of unsubstituted ylide **3a** to iodobenzene and *p*-methoxyiodobenzene afforded a 17:83 mixture of ylides **3a** and **3c** in a high yield; in addition, a comparable ratio (14:86) of these ylide mixtures was also produced in the rhodium(II)-catalyzed transfer of the bistriflylmethylidene group using substituted ylide **3c** (Table 3, entries 1 and 2). Thus, both transylation reactions resulted in the formation of *p*-methoxyphenyliodonium ylide **3c** as a major product with greater than 80% selectivity. Decreased selectivity (69–72%) for *p*-methyl-substituted ylide **3b** in the competitive transylation to iodobenzene and *p*-methyliodobenzene was evaluated (Table 3, entries 3 and 4). In marked contrast, competition with electron deficient *p*-chloro- and *p*-(trifluoromethyl)iodobenzene afforded the unsubstituted phenyl-

(11) For instance, *p*-nitrophenyliodonium dinitromethylide is more stable to thermal decomposition than phenyliodonium dinitromethylide, but the reverse is true for the iodonium ylides derived from dimedone. See Ref 4d.

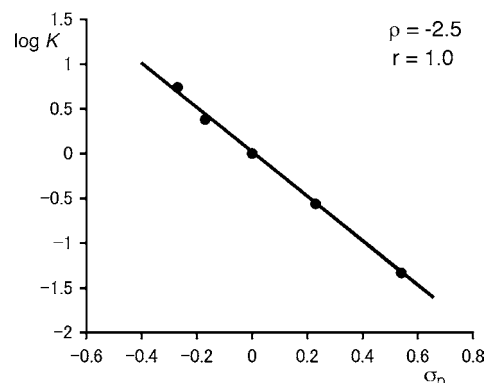
Table 3. Competitive Transylidations to Iodobenzene and a Substituted Iodobenzene^a

entry	substrate	<i>p</i> -RC ₆ H ₄ I (R)	product (yield %) ^b	ratio ^c
1	3a	MeO	3a (14) 3c (67)	17:83
2	3c	MeO	3a (13) 3c (75)	14:86
3	3a	Me	3a (27) 3b (59)	31:69
4	3b	Me	3a (23) 3b (58)	28:72
5	3a	Cl	3a (68) 3h (18)	79:21
6	3h	Cl	3a (66) 3h (19)	78:22
7	3a	CF ₃	3a (77) 3j (4)	95:5
8	3j	CF ₃	3a (86) 3j (4)	96:4

^a Reaction conditions: each iodobenzene (50 equiv)/CF₃Ph/Rh₂(OAc)₄ (5 mol %)/125 °C/10 h/Ar. ^b ¹H NMR yields. ^c Ratios of unsubstituted **3a** to a substituted iodonium ylide.

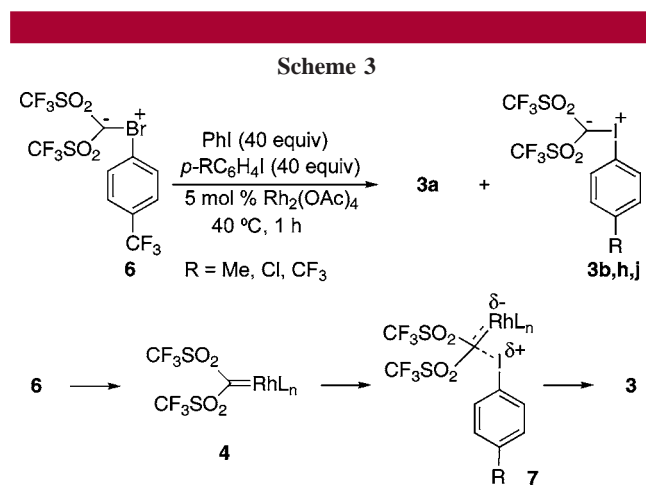
iodonium ylide **3a** as a major product with 78–79% and 95–96% selectivity, respectively. These results clearly demonstrate the reversible nature of our rhodium(II)-catalyzed transylidations between arylidonium ylides **3** under the conditions.

Furthermore, the results of Table 3, showing similar ratios of the ylide products **3** in each set of the competitive rhodium(II)-catalyzed transylidations to two competing substrates, most likely indicate that equilibrium is established under the conditions, and the ratios of the ylides **3** reflect the differences in their thermodynamic stabilities. Thus, the equilibrium constants *K* between unsubstituted **3a** and substituted arylidonium ylides **3** were estimated from their average ratios (Table 3): **3c** (*p*-MeO), 5.5; **3b** (*p*-Me), 2.4; **3a** (H), 1.0; **3h** (*p*-Cl), 0.27; **3j** (*p*-CF₃), 0.047. A Hammett plot (Figure 1) showed an excellent correlation of log *K* with substituent constants σ_p and gave a ρ value of -2.5 ($r = 1.0$).¹² These results clearly demonstrate that the thermo-

Figure 1. Hammett plot of log *K* vs σ_p constants.

dynamic stability of ylides **3** is mostly determined by the electronic nature of *para* substituents of the aromatic ring: the stability of arylidonium ylides **3** increases with the increasing electron-donating nature of the *para* substituents, which probably decreases the positive charge localized on the iodine(III) atom to some extent.

The large negative ρ value (-2.5) evaluated here can be compared with that ($\rho = -0.91$) reported for the competitive rhodium(II)-catalyzed carbenoid transfer from arylbromonium ylide **6** to aryl iodides at 40 °C (Scheme 3),⁸ in which

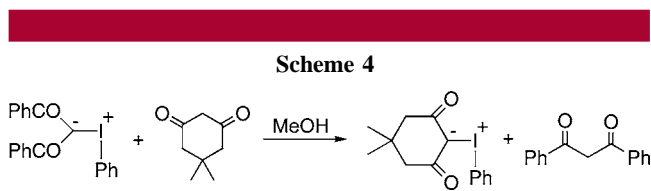


a relatively small positive charge is assumed to be developed on the iodine atom in the product-determining transition state **7**. At 40 °C, no catalyzed transylidation between arylidonium ylides **3** takes place.

Intrinsically, a partial positive charge develops on the central iodine atom in hypervalent three-center four-electron bonding of aryl- λ^3 -iodanes (ArIXY).¹³ Therefore, it seems reasonable to assume that this type of electronic effect of

substituents on the aromatic ring would contribute to determine the thermodynamic stability of all of the aryl- λ^3 -iodanes to some extent.

Interesting examples of a reverse type of transylidation reaction, where a phenyliodonium ylide transfers its phenyl- λ^3 -iodanyl group (PhI⁺) to an active methylene compound, have been reported (Scheme 4).^{5b,14} In other words, this is a



ligand exchange reaction on the iodine(III) atom.^{13,15} Here, the carbon acid (PhCOCH₂COPh) liberated from the initial iodonium ylide must be less acidic than the active methylene compound (in this case, dimedone).^{4c} Such transylidation reactions also allow at least a qualitative assessment of relative iodonium ylide stabilities.^{4d}

In conclusion, we have shown unambiguous experimental evidence for the intermolecular transylidation between arylidonium ylides under rhodium(II)-catalyzed conditions. The reaction provides a new tool for the synthesis of iodonium ylides with a variety of aryl- λ^3 -iodanyl groups that show various degrees of leaving group ability.¹ The relative thermodynamic stabilities of arylidonium ylides were evaluated.

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Supporting Information Available: Typical experimental procedures and spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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