

Synthesis of *trans*-4,4'-diiodostilbene and other symmetrical *trans*-stilbenes by Heck reaction of arenediazonium salts with vinyltriethoxysilane

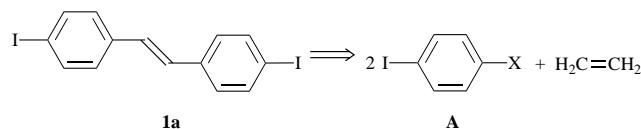
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With anilines as the starting materials, a facile new synthesis of symmetrical *trans*-stilbenes, in particular of *trans*-4,4'-diiodostilbene, by (double) Heck reaction of arenediazonium salts with vinyltriethoxysilane is described.

Introduction

In a program directed towards synthesis of poly(*p*-phenylenevinylene)s,¹ we required an efficient preparation of *trans*-4,4'-diiodostilbene **1a** that would be amenable to large-scale synthesis. Although **1a** has been described in a few patents, the open literature provided only a single report of its synthesis,² a low-yielding multi-step procedure unsuitable for our purpose. We have therefore looked for a short, alternative method which would be high-yielding and have potential for scale-up. Towards this end, after a McMurry-coupling strategy³ and Wittig methodologies had been discarded for economic reasons (the high cost of *p*-iodobenzaldehyde), it occurred to us that **1a** could be easily synthesized by a (double) Heck reaction of a *p*-IC₆H₄X derivative (**A**) with ethylene, provided that **A** preferentially reacted *via* its X-nucleofuge (Scheme 1). However, iodoarenes



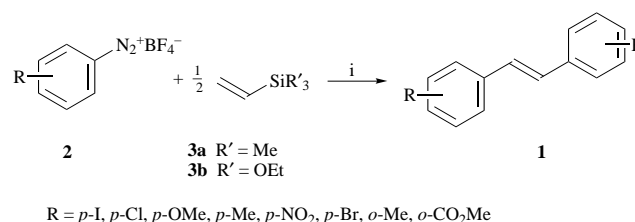
are one of the most reactive aromatic components in Heck reactions, and to find a suitable X-nucleofuge (in **A**) which would preferentially react over the iodide was difficult. Fortunately, arenediazonium salts provided a potential solution to this problem. Thus, based on the fact that Heck reactions of *p*-bromo- and *p*-iodo-arenediazonium salts occur preferentially at the diazonium end,⁴ *p*-IC₆H₄N₂⁺BF₄⁻ made an ideal choice for **A** in the above retrosynthetic scheme. Moreover, *p*-iodoaniline, which is the precursor to this salt, is readily available through simple iodination of aniline thereby providing additional impetus to the above strategy. That *p*-iodophenyldiazonium tetrafluoroborate indeed leads to **1a** *via* a (double) Heck reaction on an ethylene equivalent and that this procedure can be extended to several other arenediazonium salts to provide a new general synthesis of symmetrical *trans*-stilbenes is described in this paper.

Results and discussion

A (double) Heck reaction strategy for stilbene synthesis has recently been explored by Heitz *et al.*,⁵ using halogenoarenes and ethylene gas in a 2:1 stoichiometry which however showed that the reaction is not entirely regioselective producing varying amounts of 1,1-diarylethylenes as side-products. Moreover, a controlled use of ethylene gas is required for these reactions which called for special experimental set-ups. In view of these problems, we searched for an ethylene equivalent which could

be easily handled and at the same time, would provide better regioselectivity in our proposed (double) Heck reaction with arenediazonium salts. In this regard, vinyl acetate,⁶ a popular ethylene-equivalent for Heck reactions with aryl halides, was first tried which however failed to produce any characterizable products. In a separate study, it was later revealed that reactions of arenediazonium salts with a full equivalent of vinyl acetate (or a vinyl ether) caused extensive decomposition of the diazonium salts. Finally, after much study, vinyltributylstannane^{7a} and vinyltrimethylsilane **3a**^{7b} were found to be the most suitable ethylene equivalents for Heck reaction with arenediazonium salts, out of which the latter was preferred for the present purpose in order to avoid the toxic stannane.

In the event, Heck reaction of *p*-IC₆H₄N₂⁺BF₄⁻ **2a** with **3a** (0.5 equiv.) under our recently described alcoholic reaction conditions [2% Pd(OAc)₂, MeOH]^{4c} produced a typically fast reaction (30 min) at room temperature giving rise to **1a** in 62% yield after crystallization. The reaction was found to be highly regioselective, since none of the corresponding 1,1-diarylethylene isomer could be detected (¹H NMR) in the crude product.† However, because of the high cost and volatility of vinyltrimethylsilane, we subsequently opted for the much cheaper and higher boiling vinyltriethoxysilane **3b** which turned out to be an equally effective ethylene equivalent, producing **1a** (60%) within 1 h in refluxing methanol (Scheme 2). We believe



Scheme 2 i, 2% Pd(OAc)₂, MeOH, 60 °C, 1 h

that, in these reactions, **1a** is presumably formed as a result of two individual Heck reactions: first, the reaction of vinylsilane (**3a** or **3b**) with the salt **2a** (1 equiv.) leads to the *in situ* formation of *p*-iodo-silylstyrene and/or -styrene^{7b} and the latter then undergoes a second Heck reaction with the remaining equivalent of **2a** to form the product stilbene.⁸ Interestingly, reaction of **2a** with a full equivalent of vinyltrimethylsilane also produced **1a** (*ca.* 45%) in an exothermic reaction at room temperature which indicates that the second Heck reaction between the arenediazonium salt and *in situ* formed silylstyrene and/or

† In their ¹H NMR spectra,⁵ vinyl protons of 1,1-diarylethylenes usually appear around δ 5.0–5.5 whereas those of 1,2-diarylethylenes appear around δ 6.8–7.3.

Table 1 Preparation of *trans*-stilbenes **1** (Scheme 2)

Entry	R	Diazonium salt 2	Vinylsilane 3	Stilbene 1	Yield (%)
1	<i>p</i> -I	2a	3a	1a	62 ^a
2	<i>p</i> -I	2a	3b	1a	60
3	<i>p</i> -Cl	2b	3b	1b	55
4	<i>p</i> -OMe	2c	3b	1c	45
5	<i>p</i> -Me	2d	3b	1d	56
6	<i>p</i> -NO ₂	2e	3b	1e	67
7	<i>p</i> -Br	2f	3b	1f	72
8	<i>o</i> -Me	2g	3b	1g	46
9	<i>o</i> -CO ₂ Me	2h	3b	1h	68

^a At 25 °C for 30 min.

styrene is perhaps faster than the initial reaction of vinylsilane with the arenediazonium salt. This new synthesis of diiodostilbene is attractive on several counts of efficiency: it is convergent, occurs under mild and operationally simple conditions and uses readily available, cheap starting materials thus making it ideally suited for large-scale adaptations.

The relative ease and high efficacy of the above (double) Heck reaction encouraged us to seek for broader synthetic ramifications. Thus, if generalized, it promised a facile new aniline-based synthetic route to symmetrical stilbenes *via* a methodology that would be much superior to the existing repertoire for stilbene synthesis. Towards this goal, a number of diversely substituted arenediazonium salts **2b–h** were subjected to (double) Heck reaction with **3b** (0.5 equiv.) which, most gratifyingly, produced the corresponding *trans*-stilbenes **1b–h** under the same alcoholic reaction conditions described above (Scheme 2). The yields of these reactions are fairly good (45–72%) (Table 1) considering that they reflect the overall percentages from two individual Heck reactions. Although steric effects are marginal in the above reactions, electronic effects are quite evident from the fact that higher yields were obtained with arenediazonium salts having electron-withdrawing substituents. Significantly, by virtue of the neutral conditions of a Heck reaction, ester-containing stilbenes *e.g.* **2h**, which would be otherwise difficult to prepare *via* organometallic techniques, can be synthesized by this method in high yields. Formation of 4,4'-dinitrostilbene **1e** (67%), from the *p*-nitro salt **2e**, is also quite significant since this salt (and other nitro-containing diazonium salts) has so far resisted all attempts at its Heck reaction with acrylates.^{4e,d} Again, due to the superior Heck reactivity of the diazonium nucleofuge, the *p*-bromo salt **2f** gave rise to 4,4'-dibromostilbene **1f**⁹ which, like **1a**, is also a potentially useful synthon for poly(*p*-phenylenevinylene) synthesis.

In summary, a new aniline-based synthesis of symmetrical *trans*-stilbenes has been developed by (double) Heck reaction of arenediazonium salts with vinyltriethoxysilane. The methodology scores over the McMurry coupling and Wittig condensations in terms of ready availability of starting materials (anilines are more readily available than the corresponding aldehydes) and operational simplicity. Other attractive features are relatively fast reactions, good yields under mild conditions and regioisomerically pure products, thus providing a far better alternative to the existing stilbene syntheses including those by (double) Heck reaction of aryl halides with ethylene or vinyl acetate. Most significantly, by virtue of the superior Heck reactivity of the diazonium nucleofuge over the bromide and iodide, the present methodology allows for a facile synthesis of 4,4'-dibromo- and, in particular, 4,4'-diiodo-stilbene which are potentially useful components for the synthesis of poly(*p*-phenylenevinylene)s.

Experimental

Melting points are uncorrected. ¹H NMR spectra were recorded either on a Hitachi R-600 (60 MHz) or on a JEOL

FX-100 (100 MHz) spectrometer. LP refers to light petroleum (60–80 °C fraction). Arenediazonium tetrafluoroborates **2a–h**, prepared according to literature procedures,¹⁰ were purified by re-precipitation from an acetone solution with diethyl ether just prior to use.

Typical procedure for (double) Heck reaction of arenediazonium salts with vinyltriethoxysilane

Preparation of *trans*-4,4'-diiodostilbene 1a. Pd(OAc)₂ (15 mg, 0.06 mmol) was added to a mixture of *p*-iodophenyldiazonium tetrafluoroborate **2a**¹⁰ (0.99 g, 3.10 mmol) and vinyltriethoxysilane **3b** (0.29 g, 1.55 mmol) in MeOH (10 cm³) and the mixture was heated under reflux for 1 h. After being cooled to room temperature, it was filtered through Celite, diluted with water and extracted with chloroform (3 × 25 cm³) [Note: a large volume of chloroform should be used since the product is sparingly soluble in this solvent]. The combined extracts were washed with water, dried (Na₂SO₄) and evaporated. The residue was reprecipitated from a chloroform solution with LP to provide **1a** (0.81 g, 60%); mp 255–256 °C (lit.,² mp 259–260 °C); δ_H(CDCl₃) 7.0 (2 H, s), 7.24 (4 H, d, *J* 8) and 7.66 (4 H, d, *J* 8).

Representative physical data for **1b–h** prepared by the above typical procedure are as follows. **1b**: yield 55%; mp 170–172 °C (from LP) (lit.,^{11a} mp 173–174 °C); δ_H(CDCl₃) 7.0 (2 H, s) and 7.50 (8 H, s).

1c: Yield 45%; mp 212–213 °C (from LP) (lit.,^{11b} mp 214–215 °C); δ_H(CDCl₃) 3.76 (6 H, s), 6.75 (4 H, d, *J* 9), 6.82 (2 H, s) and 7.35 (4 H, d, *J* 9).

1d: Yield 56%; mp 178–180 °C (from LP) (lit.,^{11c} mp 179–180 °C); δ_H(CDCl₃) 2.36 (6 H, s), 7.0 (2 H, s) 7.10 (4 H, d, *J* 10) and 7.42 (4 H, d, *J* 10).

1e: Yield 67%; mp 286–287 °C (from CH₂Cl₂-LP) (lit.,^{11d} mp 288 °C); δ_H([²H₆]-DMSO) 7.64 (2 H, s), 7.88 (4 H, d, *J* 10) and 8.22 (4 H, d, *J* 10).

1f: Yield 72%; mp 214–215 °C (from CH₂Cl₂-LP) (lit.,^{11e} mp 215–216 °C); δ_H(CDCl₃) 7.03 (2 H, s) and 7.26–7.55 (8 H, m).

1g: Yield 46%; mp 80–82 °C (from LP) (lit.,^{11f} mp 83 °C); δ_H(CDCl₃) 2.43 (6 H, s) and 7.03–7.56 (10 H, m).

1h: Yield 68%; mp 99–100 °C (from LP) (lit.,^{11g} mp 100–101.5 °C); δ_H(CDCl₃) 3.82 (6 H, s) and 7.09–7.89 (10 H, m).

Acknowledgements

CSIR is thanked for a grant-in-aid (01/1371/EMR-II/95). S. K. S. thanks Jadavpur University for a Junior Research Fellowship.

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Paper 7/05652D
Received 4th August 1997
Accepted 2nd September 1997