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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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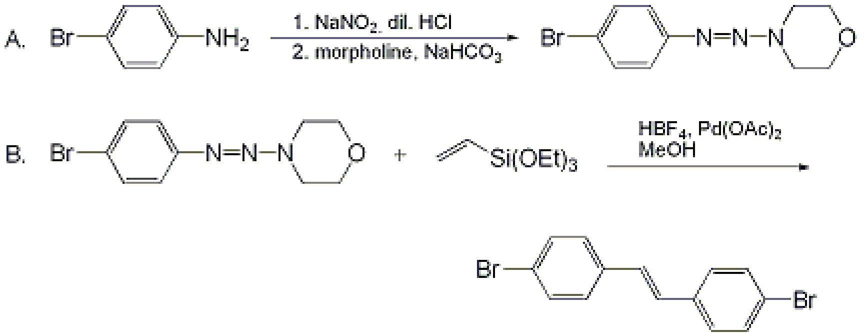
SYNTHESIS OF SYMMETRICAL trans -STILBENES BY A DOUBLE HECK REACTION OF (ARYLAZO)AMINES WITH VINYLTRIETHOXYSILANE: trans-4,4'-DIBROMOSTILBENE

[Benzene, 1,1'-(1,2-ethenediyl)bis[4-bromo-, (E)- using Silane, ethenyltriethoxy-]



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Checked by Kimberly Savary and Edward J. J. Grabowski.

1. Procedure

A. 4-[(Bromophenyl)azo]morpholine . In a 500-mL Erlenmeyer flask equipped with a magnetic stirring bar are placed 4-bromoaniline (15.0 g, 87 mmol , Note 1) and 6 N hydrochloric acid (HCl), 36.4 mL, 210 mmol) and the mixture is warmed on a water bath to make a clear solution. It is cooled to 0°C to produce a heavy precipitate. A solution of sodium nitrite (6.30 g, 91 mmol) in water (10 mL) is added dropwise over 10 min. Stirring is continued at 0°C for 20 min (Note 2), and morpholine (8.3 g, 9.0 mL, 96 mmol) is added dropwise to the above solution over 10 min. Water (100 mL) is added followed by the dropwise addition of 10% aqueous sodium bicarbonate solution (130 mL) (Note 3). After the solution is stirred for a further hour, the precipitated solid is filtered, washed with water and dried in air. The solid is dissolved in hot light petroleum (60-80 fraction) (80 mL) and treated with activated charcoal (1.5 g). The mixture is filtered while hot and the filtrate concentrated to ca. 40 mL. Upon cooling to room temperature, shiny crystals of the pure triazene are obtained. The mother liquor is concentrated to give a second crop of crystals (combined yield 20.3 g, 85%, Notes 4, 5).

B trans-4,4'-Dibromostilbene . A 500-mL round-bottomed flask equipped with a magnetic stirring bar is charged with the above triazene (14.3 g, 53 mmol) and methanol (125 mL). The stirred solution is cooled to 0°C and 40% tetrafluoroboric acid (HBF_4, 23 mL, 106 mmol) is added dropwise over 10 min. After the addition is complete, the ice bath is removed and the reaction brought to room temperature. It is stirred for an additional 10 min (Note 6) and palladium acetate [$Pd(OAc)_2$, 0.12 g, 0.53 mmol] is added followed by the dropwise addition of a solution of vinyltriethoxysilane (4.94 g, 5.5 mL, 26 mmol) in methanol(10 mL). A second lot of $Pd(OAc)_2$ (0.12 g, 0.53 mmol) is added and stirring continued for a further 30 min at room temperature (Note 7). The mixture is warmed to 40°C for 20 min and finally heated under reflux for 15 min (Note 8). The solution is concentrated under reduced pressure to half its volume and water (150 mL) is added. The precipitated solid is filtered, washed with water and dried in air. It is then boiled with toluene (125 mL) and filtered while hot. The filtrate is concentrated to ca. 70 mL, warmed to 70°C and light petroleum (30 mL) is added. Upon cooling to room temperature, the product crystallizes (4.20 g). Concentration of the mother liquor gives an additional crop (0.70 g) of the product (combined yield 4.90 g, 46.5%, Note 9).

2. Notes

1. 4-Bromoaniline (Lancaster Laboratories), morpholine (Lancaster Laboratories), vinyltriethoxysilane (Lancaster Laboratories), palladium acetate (Arora-Mathey) and 40% HBF_4 (Central Drug House) were

used as received.

2. At this point a clear solution is obtained.

3. *Caution: Vigorous evolution of carbon dioxide occurs*. The product began to precipitate. The checkers used 1 N sodium hydroxide (NaOH, approximately 120 mL to pH≈7 at 0-10°C) to effect neutralization and avoid difficulties with carbon dioxide evolution.

4. *Caution: All 1-aryl triazenes are toxic and direct hand contact should be avoided*. The checkers used hexane for the recrystallization.

5. The product showed the following physical data: mp 87-88°C (lit.[2] mp 89.5-90°C); IR ($CHCl_3$) cm^{-1}: 1100, 1210, 1345, 1430, 1480, 3010 ; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.76-3.87 (AA'BB', 8 H), 7.29-7.48 (AA'BB', 4 H) ; Anal. Calcd for $C_{10}H_{12}BrN_3O$: C, 44.47; H,4.44; N,15.56. Found: C, 44.22; H, 4.38; N, 15.50.

6. The solution became clear at this stage.

7. Some of the product, as it formed, precipitated.

8. Inferior yields were obtained when the reaction is heated directly under reflux without being held at 40°C for ca. 20 min.

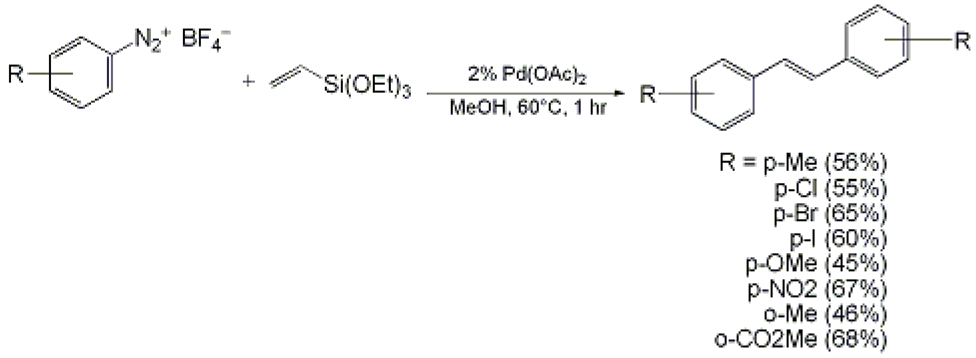
9. The product showed the following physical data: mp 214–215°C (lit.[3] mp 215–216°C); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.01 (s, 2 H), 7.35 (d, 4 H, J = 6.9), 7.47 (d, 4 H, J = 6.9) .

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Stilbenes are an important class of chromophores that have found various applications in molecular photonics and optoelectronics.[4] Symmetrical trans-stilbenes are classically prepared via oxidative dimerization of benzylic halides, which usually require strongly basic conditions and high reaction temperatures.[5] More recent methods include McMurry-coupling of aromatic aldehydes,[6] Wittig condensations and double Heck reactions of haloarenes with ethylene.[7] The latter procedure, however, is inconvenient since it requires a measured amount (half equivalent) of ethylene gas under autoclave conditions. Moreover, a double Heck reaction of aryl bromides and iodides with ethylene invariably produces some of the undesired 1,1-diarylethylene regioisomer (up to 20%). The stilbene synthesis described here is based on the submitters' recent report on double Heck reactions of arenediazonium salts with vinyltriethoxysilane (Scheme 1).[8] The procedure has been suitably modified so that the arenediazonium salt is generated in situ from 1-aryltriazene, thus avoiding direct handling of the diazonium salt.[9]



Synthesis of symmetrical stilbenes via a double Heck reaction of arenediazonium salts with vinyltriethoxysilane is attractive on several counts: Ready availability of starting materials (anilines are more readily available in a diverse substitution pattern than are aryl halides and aldehydes); Mild reaction conditions that tolerate a number of functional groups (e.g., NO_2, CO_2R); Strategic use of vinyltriethoxysilane as a cheap and easily handled ethylene equivalent; And operational simplicity (alcoholic reaction medium, ligandless Pd-catalyst, no additives). Most significantly, by virtue of the superior Heck reactivity of the diazonium nucleofuge over bromide (and even iodides),[10,11] the present methodology allows for a facile synthesis of 4,4'-dibromo- (and 4,4'-diiodo-) stilbenes, which would otherwise be difficult to synthesize (impossible for the diiodo derivative) via the double Heck reaction of haloarenes with ethylene. Recently, the submitters have also described the double Heck reaction of bisarenediazonium salts with vinyltriethoxysilane for the synthesis of poly(1,4-biarylenevinylenes).[12]

The dibromo- (and diiodo-) stilbenes are potentially useful monomers for the synthesis of poly(*p*-phenylenevinylenes) via poly-Heck or poly-Suzuki coupling reactions.[13]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Vinyltriethoxysilane: ALDRICH:
Triethoxyvinylsilane:

Silane, triethoxyvinyl- (8);
Silane, ethenyltriethoxy- (9); (78-08-0)

trans-4,4'-Dibromostilbene:
Stilbene, 4,4'-dibromo-, (*E*)- (8);
Benzene, 1,1'-(1,2-ethenediyl)bis[4-bromo-, (*E*)- (9); (18869-30-2)

4-Bromoaniline:
Aniline, p-bromo- (8);
Benzenamine, 4-bromo- (9); (106-40-1)

4-[(4-Bromophenyl)azo]morpholine:
Morpholine, 4-[(4-bromophenyl)azo]- (14); (188289-57-8)

Sodium nitrite:
Nitrous acid, sodium salt (8, 9); (7632-00-0)

Morpholine (8, 9); (110-91-8)

Tetrafluoroboric acid:
Borate (1-), tetrafluoro-, hydrogen (8, 9); (16872-11-0)

Palladium acetate:
Acetic acid, palladium(2+) salt (8, 9); (3375-31-3)