A Novel Synthesis of β,β-Dibromostyrenes

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Abstract: A new simple and efficient transformation of aromatic aldehydes to β,β-dibromostyrenes and arylbromoacetylenes is described. The olefination procedure was conducted under mild conditions and in good yields.

Key words: aromatic aldehydes, olefination, dibromostyrenes, copper-carbene complexes, carbon tetrabromide

Olefination of carbonyl compounds, that is, C=O/C=CXY transformation, is one of the fundamental procedures for the preparation of substituted alkenes.1 The Wittig reaction and its modifications are the most widely used ways for this transformation.2 However, the necessity to use equimolar amounts of phosphoric reagents is a significant disadvantage. Therefore, new, preferably, catalytic approaches for the olefination are desirable in modern organic synthesis.

Recently, we elaborated a novel non-Wittig approach towards olefination.3,4 The proposed method was based on the new redox reaction between N-unsubstituted hydrazones of aromatic aldehydes and carbon tetrachloride (Scheme 1). The reaction took place under copper catalysis in the presence of aqueous ammonia to give the corresponding dichloroalkenes in high yields.4,5

Scheme 1

The proposed transformation represented a new general type of reaction for the formation of new C=C bonds. The variations of the haloalkanes permitted the preparation of different types of alkenes. For example, freons CF3CCl3,6 CF3Cl–CFCl2,6 and bromoform7 can be used for stereoselective preparation of the corresponding alkenes. It should be noted that this new procedure is air- and moisture-sensitive. Mild conditions and the simplicity of the technique are favourable features of the reaction.

This paper presents the results of the use of carbon tetrabromide in this reaction. We found that CBr4 reacted with hydrazones 1a–i in a similar way to give as target products the corresponding β,β-dibromostyrenes 2a–i (Scheme 2). Moreover, the corresponding sym-azines were also isolated as side products.

Scheme 2

β,β-Dibromostyrenes are important reagents in modern organic synthesis being synthetic precursors of terminal and unsymmetrical acetylenes,8,9 bromoacetylenes,10,11 and fused heterocycles.12 Recently, various cross-coupling reactions with substituted β,β-dibromostyrenes were described.13 In the last decade new methods for stereoselective reduction of dibromoalkenes into E-14,15 and Z-isomers16 of terminal vinyl bromides were elaborated.

We studied the conversion of the wide range of hydrazones of aromatic aldehydes bearing various substituents in the aromatic ring to the corresponding dibromostyrenes. In general, the reactions proceeded smoothly to give the target products in good yield (Table 1).

Table 1 Synthesis of Dibromostyrenes

<table>
<thead>
<tr>
<th>Product</th>
<th>Aryl</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>4-ClC6H4</td>
<td>84</td>
</tr>
<tr>
<td>2b</td>
<td>2-ClC6H4</td>
<td>77</td>
</tr>
<tr>
<td>2c</td>
<td>4-FC6H4</td>
<td>71</td>
</tr>
<tr>
<td>2d</td>
<td>2-FC6H4</td>
<td>92</td>
</tr>
<tr>
<td>2e</td>
<td>4-BrC6H4</td>
<td>92</td>
</tr>
<tr>
<td>2f</td>
<td>4-CH3C6H4</td>
<td>87</td>
</tr>
<tr>
<td>2g</td>
<td>4-CF3C6H4</td>
<td>57</td>
</tr>
<tr>
<td>2h</td>
<td>2-CF3C6H4</td>
<td>81</td>
</tr>
<tr>
<td>2i</td>
<td>4-CH3-CH3C6H4</td>
<td>79</td>
</tr>
</tbody>
</table>

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In some cases, however, olefination was accompanied with the formation of the corresponding bromoacetylenes (Scheme 3). Substrates containing strong electron-withdrawing groups or sterically hindered hydrazones were prone to conversion to the corresponding bromoacetylenes (Table 2).

![Scheme 3](image)

**Scheme 3**

### Table 2  Formation of the Mixture of Dibromoalkenes and Bromoacetylenes

<table>
<thead>
<tr>
<th>Aryl</th>
<th>Ratio 2:3</th>
<th>Total Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-O$_2$NC$_6$H$_4$</td>
<td>1:1</td>
<td>78</td>
</tr>
<tr>
<td>2-O$_2$NC$_6$H$_4$</td>
<td>4:1</td>
<td>50</td>
</tr>
<tr>
<td>2-BrC$_6$H$_4$</td>
<td>4:3</td>
<td>77</td>
</tr>
<tr>
<td>2,6-Cl$_2$C$_6$H$_3$</td>
<td>5:6</td>
<td>30</td>
</tr>
</tbody>
</table>

* Determined from $^1$H NMR data.

A slight modification of the technique permitted the one-pot preparation of arylbromoacetylenes 3k–m without isolation of dibromostyrenes. After nitrogen evolution had completed, the reaction mixture was treated with DBU; as a result bromoacetylenes were prepared in pure form (Table 3).

### Table 3  Synthesis of Aryl bromoacetylenes

<table>
<thead>
<tr>
<th>Product</th>
<th>Aryl</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3k</td>
<td>2-O$_2$NC$_6$H$_4$</td>
<td>66</td>
</tr>
<tr>
<td>3l</td>
<td>2-BrC$_6$H$_4$</td>
<td>71</td>
</tr>
<tr>
<td>3m</td>
<td>2,6-Cl$_2$C$_6$H$_3$</td>
<td>43</td>
</tr>
</tbody>
</table>

Previously, we proposed a general mechanism of this new reaction (Scheme 4). The key intermediate is the copper-carbenoid complex I, formed in the reaction of copper (II) with hydrazone via the corresponding diazoalkane. Similar copper-carbenoid complexes are universally accepted as reactive intermediates in many copper-catalysed reactions, addition of diazoalkanes to C=C bond, and ylides generation. Some stable imidazolyl- and thiazolyl-carbenoid complexes of Cu were recently isolated.

Intermediate I reacts with a molecule of CBr$_4$ to give the target alkene and to regenerate the copper(II) (inside the cycle). Another type of transformation of I is the reaction with diazoalkane to form sym-azine (outside the cycle). The copper oxidation step completes the outside catalytic cycle.

![Scheme 4](image)

**Scheme 4**

The corresponding azines and bromof orm were detected by $^1$H NMR investigations of reaction mixture.

In summary, we have elaborated a new non-Wittig approach to $\beta,\beta$-dibromostyrenes. Mild conditions, simplicity of the experimental technique and high yields of products are remarkable advantages of the presented method.

NMR spectra were recorded on a Varian VX-400 and Bruker AM 400C spectrometers in CDCl$_3$ with TMS as an internal standard. IR spectra were obtained with UR-20 spectrometer. Merck 60F$_254$ plates were used for analytical TLC chromatography. Column chromatography was performed on silica gel (63–200 mesh, Merck). Mass-spectra were recorded on a HP59890 mass spectrometer with the 5989x-G detector.

Hydrazones of aromatic aldehydes 1a–m were prepared as previously described.

### Dibromostyrenes: General Procedure

Aq NH$_3$ (25%, 3.33 mL) and Cu$_2$Cl$_2$ (100 mg, 1 mmol) were added to a solution of the hydrazone (10 mmol) in DMSO (10 mL). Then, a solution of CBr$_4$ (9.9 g, 30 mmol) in DMSO (20 mL) was added dropwise over 10 min, maintaining the temperature at about 0°C. The reaction mixture was stirred for 4 h, and quenched with H$_2$O (300 mL). The reaction products were extracted with CH$_2$Cl$_2$ (3 ¥ 50 mL), extracts were dried (Na$_2$SO$_4$), CH$_2$Cl$_2$ was evaporated, and the residue was purified by column chromatography (hexane).

The known compounds 2a, 2f, 2i were identified by comparison of their spectral data with those described in the literature.

#### 1-Chloro-2-(2,2-dibromovinyl)benzene (2b)

Colourless oil; R$_t$ = 0.55 (hexane).

IR: 1610 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): δ = 7.22–7.28 (m, 2 H, Ar), 7.35–7.39 (m, 1 H, Ar), 7.54 (s, 1 H, –CH=), 7.60–7.63 (m, 1 H, Ar).

$^1$C NMR (CDCl$_3$): δ = 92.76 (–CBr$_2$), 126.44, 129.36, 129.60, 129.96, 132.95, 133.94, 134.62.
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1-(2,2-Dibromovinyl)-4-fluorobenzene (2c)
Colourless oil; $R_f = 0.60$ (hexane).
IR: $1620 \text{ cm}^{-1}$.
$^1H$ NMR (CDCl$_3$): $\delta = 6.97$ (dd, 2H, $J = 8.6, 8.6$ Hz, Ar), 7.33 (s, 1H, $-\text{CH}=)$, 7.43 (dd, 2H, $J = 8.6, 4.3$ Hz, Ar).
$^{13}C$ NMR (CDCl$_3$): $\delta = 90.93 (=\text{CBr})$, 115.10 ($J = 21.6$ Hz, C-3,5), 130.92 ($J = 7.6$ Hz, C-2,6), 131.98 (C-1), 136.36 ($-\text{CH}=)$, 163.20 ($J = 248.7$ Hz, C-F).

Anal. Calcd for C$_8$H$_5$Br$_2$F: C, 34.32; H, 1.80. Found: C, 34.16; H, 1.76.

1-(2,2-Dibromovinyl)-2-fluorobenzene (2d)
Colourless oil; $R_f = 0.60$ (hexane).
IR: $1620 \text{ cm}^{-1}$.
$^1H$ NMR (CDCl$_3$): $\delta = 6.97$ (dd, 1H, $J = 9.7, 8.7$ Hz, Ar), 7.15 (dd, 1H, $J = 7.9, 7.6$ Hz, Ar), 7.32 (m, 1H, Ar), 7.54 (s, 1H, $-\text{CH}=)$, 7.76 (dd, 1H, $J = 7.9, 7.6$ Hz, Ar).
$^{13}C$ NMR (CDCl$_3$): $\delta = 92.70 (=\text{CBr})$, 107.76 ($J = 94.6$ Hz, C-1), 116.19 ($J = 21.4$ Hz, Ar), 124.51 (Ar), 129.94 (Ar), 130.73 (Ar), 131.05 ($J = 9.2$ Hz, $-\text{CH}=)$, 160.34 ($J = 250.3$ Hz, C-F).

Anal. Calcd for C$_8$H$_5$Br$_2$F: C, 34.32; H, 1.80. Found: C, 34.45; H, 1.76.

1-(2,2-Dibromovinyl)-2-fluorobenzene (2d)
Colourless oil; $R_f = 0.60$ (hexane).
IR: $1620 \text{ cm}^{-1}$.
$^1H$ NMR (CDCl$_3$): $\delta = 7.06$ (dd, 1H, $J = 9.7, 8.7$ Hz, Ar), 7.37 (s, 1H, $-\text{CH}=)$, 7.46 (d, 2H, $J = 8.7$ Hz, Ar).
$^{13}C$ NMR (CDCl$_3$): $\delta = 90.51 (=\text{CBr})$, 122.57, 129.82, 131.54, 134.03, 135.62.

MS (EI, 70 eV): $m/z$ (%) = 226 (7) [$M^+$], 170 (13) [C$_7$H$_5$Br*], 90 (100) [C-H$_2$].

Anal. Calcd for C$_7$H$_5$BrNO$_2$: C, 45.21; H, 1.78. Found: C, 45.27; H, 2.01.

1-Bromo-2-(bromoethynyl)benzene (3l)
Colourless oil; $R_f = 0.55$ (hexane).
$^1H$ NMR (CDCl$_3$): $\delta = 7.17$ (ddd, 1H, $J = 8.2, 8.1, 1.8$ Hz, Ar), 7.23 (dd, 1H, $J = 8.2, 8.1, 1.4$ Hz, Ar), 7.44 (dd, 1H, $J = 8.1, 1.8$ Hz, Ar), 7.54 (dd, 1H, $J = 8.2, 1.4$ Hz, Ar).
$^{13}C$ NMR (CDCl$_3$): $\delta = 54.91 (=\text{CBr})$, 78.82 (=C–Ar), 125.77, 127.03, 129.83, 130.77, 132.47, 133.93.

MS (EI, 70 eV): $m/z$ (%) = 260 (68) [$M^+$], 179 (22) [$M^+–Br$], 100 (63) [$M^+–2Br$], 76 (100) [$M^+–2Br–2C$].


2-(Bromoethynyl)-1,3-dichlorobenzene (3m)
Colourless oil; $R_f = 0.55$ (hexane).
$^1H$ NMR (CDCl$_3$): $\delta = 7.17$ (t, 1H, $J = 7.8$ Hz, -CH-S), 7.29 (dd, 2H, $J = 7.8$ Hz, CH-4,6).
$^{13}C$ NMR (CDCl$_3$): $\delta = 60.99 (=\text{CBr})$, 74.40 (=C–Ar), 127.50, 129.32, 131.12, 137.95.

MS (EI, 70 eV): $m/z$ (%) = 250 (100) [$M^+$], 169 (28) [$M^+–Br$], 133 (35) [$M^+–Br–Cl$], 98 (71) [$M^+–Br–2Cl$], 74 (32) [$M^+–Br–2Cl–2C$].


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References
(21) Arduengo, A. J. III; Rasika Dias, H. V.; Calabrese, J. C.; Davidson, F. Organometallics 1993, 12, 3405.