

# A Novel Synthetic Approach to Dichlorostyrenes

Alexey V. Shastin,<sup>a</sup> Vasily N. Korotchenko,<sup>b</sup> Valentine G. Nenajdenko<sup>b,\*</sup> and Elisabeth S. Balenkova<sup>b</sup>

<sup>a</sup>Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region 142432, Russia

<sup>b</sup>Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119899, Russia

Received 14 April 2000; revised 12 June 2000; accepted 29 June 2000

**Abstract**—We found that *N*-unsubstituted hydrazones of aromatic aldehydes can be easily converted to the corresponding 1,1-dichlorostyrenes in the reaction with carbon tetrachloride using copper (I) chloride as catalyst. Factors affecting the route of the reaction and yields of the products were investigated. A proposed mechanism for the reaction is discussed. © 2000 Published by Elsevier Science Ltd.

## Introduction

The conversion of a carbonyl group into a double C–C bond is a common problem in synthetic organic chemistry. Dichlorostyrenes are widely used for the syntheses of acetylenes and chloroacetylenes as well as some other types of compounds.<sup>1,2</sup> Many approaches to the 1,1-dihalogenoalkenes synthesis such as Wittig reaction and its modifications,<sup>2,3</sup>  $\alpha$ -trichloromethylcarbinol ester reduction,<sup>4</sup> reductive coupling of polyhalogenalkanes with aromatic aldehydes<sup>5</sup> and (2+2) cycloaddition of dichloroalkenes to aldehydes have been used.<sup>6</sup>

Recently we have reported that *N*-unsubstituted hydrazones of aromatic aldehydes could be easily converted to the corresponding dichlorostyrenes by the reaction with carbon tetrachloride in the presence of copper(I) chloride (Scheme 1).<sup>7</sup> Substrates bearing both electron-withdrawing and electron-donating substituents give the target products in good yields. Besides the dichlorostyrenes the corresponding azines **3** have been isolated as side products. This reaction presents a novel, facile and convenient method for the conversion of the hydrazones of aromatic aldehydes into dichlorostyrenes.<sup>7</sup> Mild conditions (room temperature) and good yields (up to 84%) make the method be very useful for synthetic purposes.

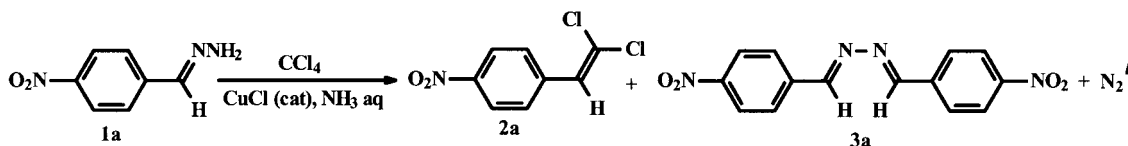
Our preliminary results show that the reaction is complicated and the yield of the dichlorostyrene depends dramatically on the reactions conditions. Here we report our investigation of the reaction optimisation in order to reach the maximal yield of the product. We investigated also the mechanism of the transformation.

## Results and Discussion

We have found that the main factors affecting the yield of dichlorostyrenes are the nature of the catalyst and its amount, the polarity and the type of solvent used and the reagent/substrate ratio. The hydrazone of *p*-nitrobenzaldehyde **1a** was used as a representative model due to its stability. In each case the isolated yield of 4-nitrodichlorostyrene **2a** was determined. Since nitrogen is formed during the reaction, its rate of evolution was used as measure of the effectiveness of the conditions and completeness of the transformation.

### Optimization of the reaction conditions

**Influence of the catalyst nature.** Our previous experiments showed that DMSO is one of the most suitable solvents for the reaction, therefore in our study DMSO was used as a



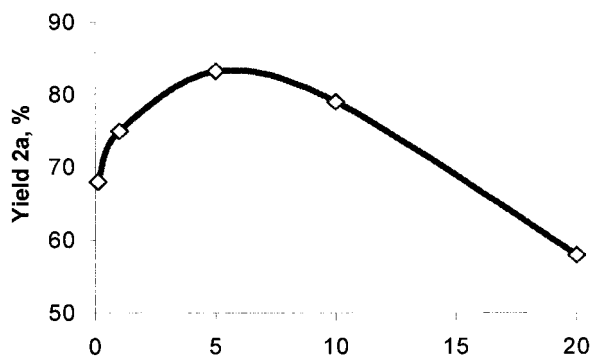
Scheme 1.

**Keywords:** catalysis; copper salts; dichlorostyrenes; hydrazones; carbon tetrachloride.

\* Corresponding author. Tel.: +7-095-939-2276; fax: +7-095-932-8846; e-mail: nen@acylium.chem.msu.ru

**Table 1.** Influence of the catalyst nature on yield of **2a**

| Catalyst   | Yield <b>2a</b> (%) |
|--|---------------------|
| CuCl   | 79                  |
| CuCl <sub>2</sub>  | 78                  |
| CoCl <sub>2</sub> ×6H <sub>2</sub> O   | 61                  |
| PdCl <sub>2</sub>  | 61                  |
| (NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ×6H <sub>2</sub> O | 20                  |
| HgCl <sub>2</sub>  | 16                  |
| Ag <sub>2</sub> SO <sub>4</sub>  | 11                  |
| NiCl <sub>2</sub> ×6H <sub>2</sub> O   | 6                   |
| MnSO <sub>4</sub> ×5H <sub>2</sub> O   | 0                   |

**Figure 1.** Yield of **2a** depending on catalyst /substrate ratio.

solvent for the determination of the optimal catalyst. Standard reaction conditions for the conversion of **1a** (0.01 mol) were a DMSO solution (10 ml) of carbon tetrachloride (0.05 mol) and aqueous ammonia (3.33 ml), all the reactions were carried out at room temperature. A gas burette was used for the measurement of the nitrogen volume for the reaction monitoring. It should be noted that the reaction does not take place without catalyst and in that case 94% of starting material **1a** was recovered. Different transition metals salts (10 mol%) were tested as catalysts. As shown in Table 1 the reaction proceeds in the presence of any metal salts (except for Mn<sup>2+</sup> salt). The best yields of styrene were found in the case of Pd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cu<sup>+</sup> salts. We found that catalytic activity estimated by the rate of N<sub>2</sub> evolution decreases in the sequence: CuCl<sub>2</sub>>PdCl<sub>2</sub>>CuCl>CoCl<sub>2</sub>. Other transition metal salts

such as Ni(II), Fe(II), Hg(II) and Ag(I) salts were found to be much less active.

To summarise these data the best catalyst (higher yield and optimal reaction rate) are copper (I and II) salts, however in the case of copper dichloride the reaction rate is too high and strong evolution of nitrogen results in some inconvenience due to foaming of the reaction mixture. On the other hand, using copper(I) chloride as a catalyst the reaction takes place in optimal time to give the best yield of the target dichlorostyrene. According to these results, copper (I) chloride was found to be the best catalyst for the procedure.

**Influence of the catalyst quantity.** In order to determine the optimal substrate/catalyst ratio we carried out the reaction using various amounts of copper(I) chloride (the other parameters were fixed the same). As is shown in Fig. 1 the optimal quantity of CuCl is about 5–10%, with any increase of the catalyst amount leading to lower yields of dichlorostyrene due to by-product formation.

**Solvent nature influence.** We have investigated the influence of the nature of the solvent on the dichlorostyrene yield and reaction rate (10 mol% copper(I) chloride as catalyst). Various solvents with different polarity and nature have been tested. The reaction proceeds rapidly and the best yield of **2a** was obtained in polar solvents with high solvating ability, characterized by the dipole moment and dielectric permeability (Table 2). We believe that the formation of a complex between the copper salt and solvent molecules plays a significant role in the catalytic activity, since in the case of hexane and benzene, which do not solvate copper ions only trace amount of the target product were isolated; similarly, no reaction occurs using halogenated solvents such as CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub>.

However, there is no direct correlation between solvent properties and the product yield. In most solvents the reaction proceeds completely (by gas evolution measurement) within 3 h to 3 days. The maximum yield of the target dichlorostyrene was obtained in DMSO solution.

**Reagent/substrate ratio.** We have studied the optimal CCl<sub>4</sub> (reagent)/substrate (hydrazone **1a**) ratio to be taken into the

**Table 2.** Influence of the nature of the solvent

| Solvent                     | Yield <b>2a</b> (%) | $\epsilon_r$ , <sup>8</sup> dielectric permeability | $\mu \cdot 10^{30}$ , (C·m), <sup>8</sup> dipole moment |
|-----------------------------|---------------------|---|---|
| Formamide                   | 48                  | 111.0   | 11.2  |
| Ethandiol                   | 59                  | 37.7  | 7.7   |
| Methyl alcohol              | 61                  | 32.66   | 5.7   |
| <i>N</i> -methylformamide   | 63                  | 182.4   | 12.9  |
| Ethyl alcohol               | 59                  | 24.55   | 5.8   |
| Isopropyl alcohol           | 53                  | 19.92   | 5.5   |
| Nitromethane                | 58                  | 35.94   | 11.9  |
| Acetonitrile                | 57                  | 35.94   | 11.8  |
| <b>DMSO</b>                 | <b>79</b>           | <b>46.45</b>  | <b>13.5</b>   |
| Sulfolane                   | 57                  | 43.3  | 16.0  |
| DMF                         | 57                  | 36.71   | 10.8  |
| <i>N</i> -methylpyrrolidone | 12                  | 32.2  | 13.6  |
| Tetramethyl urea            | 64                  | 23.6  | 11.7  |
| HMPTA                       | 47                  | 29.6  | 18.5  |
| Dimethoxyethane             | 10                  | 7.20  | 5.7   |
| THF                         | 27                  | 7.58  | 5.8   |
| Benzene                     | 12                  | 2.27  | 0.0   |
| Hexane                      | 8                   | 1.88  | 0.0   |

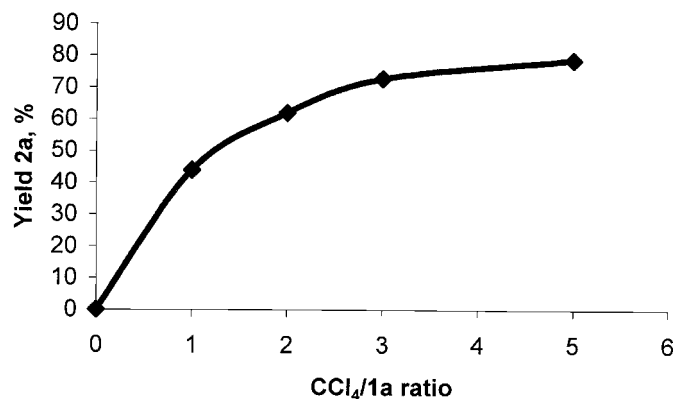


Figure 2. Dependence of yield of **2a** on CCl<sub>4</sub>/1a ratio.

Table 3. Reaction of hydrazones **1a–p** with CCl<sub>4</sub>

| Substrates, R= | a, 4-NO <sub>2</sub> | b, 3-NO <sub>2</sub> | c, 4-CN   | d, 3-CN | e, 4-Br              | f, 3-Br  | g, 4-Cl                    | h, 3-Cl |
|----------------|----------------------|----------------------|-----------|---------|----------------------|----------|----------------------------|---------|
| Yield (%)      | 2<br>79              | 67                   | 78        | 70      | 57                   | 66       | 74                         | 65      |
|                | 3<br>17              |                      | 17        |         | 40                   |          |                            |         |
| Substrates, R= | i, 2-Cl              | k, 2,6-Cl            | l, 2,4-Cl | m, H    | n, Me <sub>2</sub> N | o, 4-MeO | p, 2-OH, 5-NO <sub>2</sub> |         |
| Yield (%)      | 2<br>64              | 79                   | 62        | 27      | 26                   | 49       | 14                         |         |
|                | 3<br>15              |                      |           | 68      |                      | 44       | 80                         |         |

reaction. The procedure was carried out in DMSO solution with various amount of carbon tetrachloride. As is shown in Fig. 2 the optimal CCl<sub>4</sub>/substrate ratio is about 5. Any further increase in the carbon tetrachloride quantity does not lead to a substantially better yield of dichlorostyrene, but in the case of lower amounts of this reagent the yield of the target product decreases dramatically. Thus we found that 5 equiv. of carbon tetrachloride is optimal for the reaction procedure.

**Study of substrate nature. Preparative synthesis of 1,1-dichlorostyrenes.** Having found the optimal reaction conditions we tried to study the scope and limitations of the technique. A wide range of hydrazones<sup>9</sup> of aromatic aldehydes were converted to the corresponding dichlorostyrenes having various substituents in the aromatic ring. In most cases the reaction proceeded smoothly to give the target product in good yield. The formation of the corresponding azines **3** is the main side reaction. The total yield of these products (**2**+**3**) is nearly quantitative (Table 3). It should be noted that the purification of the styrenes is very simple since the separation of azines proceeds without any problem due to its low solubility.

It was found that the yields of dichlorostyrenes were generally better in the case of hydrazones which contain electron withdrawing groups such as nitro, cyano and halogen. In the case of the parent unsubstituted compound as well as electron rich hydrazones the yield of styrenes decreases and the formation of azines prevails over the formation of styrenes.

An abnormal result was obtained in the case of hydrazone **1p** having an electron-withdrawing group along with an electron-donating substituent. The major product was azine **3p** (yield 80%). The corresponding dichlorostyrene

**2p** was isolated in 14% yield whereas the reaction with structurally similar hydrazone **1b** gives the styrene **2b** in 67% yield.

**Influence of substituents on the reaction rate.** We investigated also the dependence of the reaction rate on aromatic ring substituents (Fig. 3). As is shown in Scheme 1 both reactions (transformation to styrene or azine) are accompanied by nitrogen evolution, however the rate of conversion is approximately in accordance with gas evolution.

As is shown in Fig. 3, at the initial moment of reaction the rate of nitrogen evolution is almost equal for the substrates bearing electron withdrawing groups such as 4-NO<sub>2</sub> and 4-CN. In the case of hydrazone **1o** containing an electron donating group (4-MeO) more rapid conversion takes place. It is known that the electron donating groups facilitate the oxidation of hydrazones whereas electron withdrawing groups deactivate.<sup>11</sup>

The hydrazone of 2,6-dichlorobenzaldehyde **1k** is much less active by comparison with other substrates. Evidently the reaction is sensitive to the steric hindrance of the substrate.

A very low nitrogen evolution rate was observed in the case of hydrazone **1p**, this abnormal result is in agreement with the predominant formation of the corresponding azine in the case of this hydrazone. As is shown in Scheme 1, the formation of azine results in the formation of half a mole of nitrogen (per mole of hydrazone) but conversion to styrene gives one molecule of nitrogen.

**Reaction mechanism.** We have found that no gas evolution and no formation of the products **2a** and **3a** took place (TLC

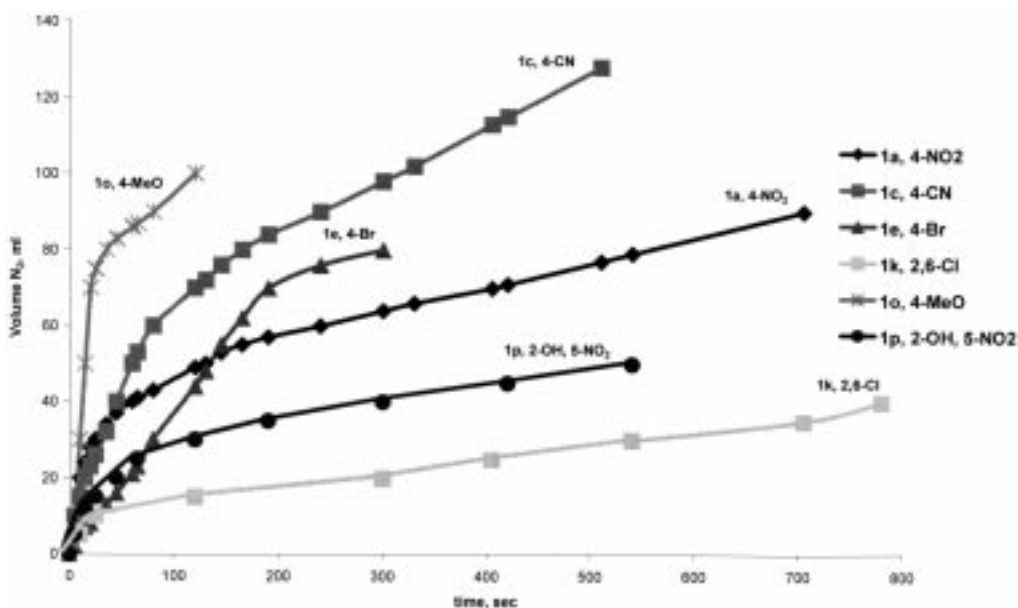


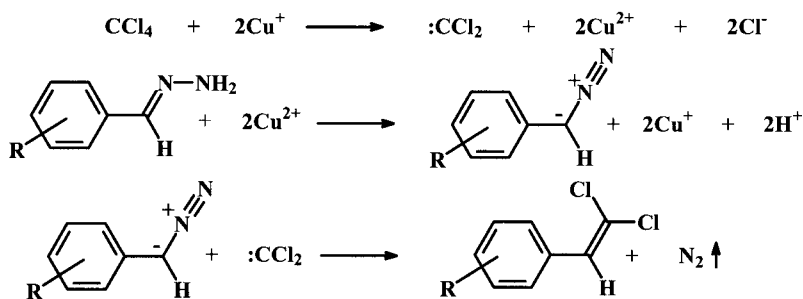
Figure 3. Gas evolution rate for different substrates.

monitoring) without copper(I) chloride catalyst or carbon tetrachloride. Therefore, we assume that the first step of the reaction is oxidation of copper(I) by carbon tetrachloride with formation of dichlorocarbene according to Assher and Vofsi.<sup>10</sup> On the other hand, it is well known that transition metals salts can convert hydrazones into the corresponding diazoalkanes.<sup>11</sup> We supposed that *p*-nitrophenyldiazomethane can be an intermediate in this transformation. The following reaction between dichlorocarbene and *p*-nitrophenyldiazomethane resulted in formation of the dichlorostyrene **2a** (Scheme 2). The reoxidation of the reduced Cu (I) to Cu (II) with  $\text{CCl}_4$  takes place to form a catalytic cycle.

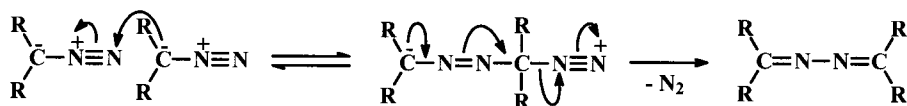
The reaction between diazoalkanes and dihalocarbenes produced from haloforms has been described previously.<sup>12</sup> The reaction mechanism was suggested to be an electrophilic attack on the carbon atom of the diazoalkane by the

carbene. The corresponding dihaloalkenes were obtained in yields 28–85%, and the authors also obtained the corresponding azines. The azine formation has been explained by interaction between two molecules of diazoalkane (Scheme 3). Only two products **2** and **3** were isolated from the reaction mixture with nearly quantitative total yield. The proposed mechanism of the reaction is in accordance with the experimental data obtained in our work.

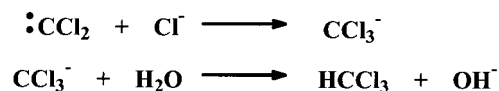
For the verification of the proposed mechanism we introduced separately prepared *p*-nitrophenyldiazomethane into the reaction. It was found that *p*-nitrophenyldiazomethane gave dichlorostyrene **2a** in 11% yield, but azine **3a** was the main product of the reaction. *p*-Nitrobenzaldehyde was isolated together with **2a** and **3a**. Probably *p*-nitrobenzaldehyde is formed by hydrolysis of *p*-nitrophenyldiazomethane followed by oxidation. Nevertheless, this results show that the system studied is rather complex.



Scheme 2.



Scheme 3.



Scheme 4.

We assume that formation of dichlorocarbene is accompanied by chloroform formation in the system (Scheme 4).

We conducted the reaction using carbon tetrachloride in DMSO- $d_6$  as solvent and after the completion of nitrogen evolution the reaction mixture was passed through a column with silica gel to remove the copper salts. In the  $^1\text{H}$  NMR spectrum an additional signal with shift 7.64 ppm was detected, the  $^{13}\text{C}$  spectrum has the signal of chloroform at 78.04 ppm. These data are in agreement with our supposition about dichlorocarbene intermediate formation.

### Conclusion

A novel synthesis of 1,1-dichloroalkenes from hydrazones of aromatic aldehydes has been elaborated. The facile and efficient technique provides the target styrenes in good or excellent yields under mild conditions.

### Experimental

#### General

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on a Varian VXR-400 and Bruker AM 400C spectrometers in  $\text{CDCl}_3$  or DMSO- $d_6$  with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Column chromatography was performed on silica gel (63–200 mesh, Merck).

#### General procedure for hydrazone preparation

Hydrazones **1a–p** were prepared as described in the literature.<sup>13</sup> An aromatic aldehyde (20 mmol) was added to the solution of 100% hydrazine hydrate (9.8 ml, 200 mmol) in ethyl alcohol (20 ml). Reaction mixture was refluxed during 3 h and cooled. The precipitate of hydrazone was filtered and recrystallized from EtOH.

The known compounds were identified by comparison of the spectral data and melting point or boiling point with described in literature.

**Hydrazone of 4-nitrophenylbenzaldehyde (1a).** Yield 92%, mp 134–135°C (lit.<sup>13</sup> 134°C).

**Hydrazone of 3-nitrophenylbenzaldehyde (1b).** Yield 87%, mp 107–108°C (lit.<sup>13</sup> 107°C).

**4-Hydrazonomethyl-benzonitrile (1c).** Yield 89%, mp 66–67°C (lit.<sup>14</sup> 66–67°C).

**3-Hydrazonomethyl-benzonitrile (1d).** The compound was obtained as colourless crystals, yield 77%, mp

83–84°C (from EtOH); IR (Nujol) ( $\nu$ ,  $\text{cm}^{-1}$ ): 1610 (C=N), 2240 (CN).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H, 2-H), 7.77 (d,  $^3J=7.8$  Hz, 1H, 4-H), 7.69 (s, 1H, CH=N), 7.61 (d,  $^3J=7.6$  Hz, 1H, 6-H), 7.49 (dd,  $^3J=7.6$  Hz,  $^3J=7.8$  Hz, 1H, 5-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.89 (C=N), 135.16 (C-3), 130.40, 129.69, 129.14 and 128.28 (C-2, C-4, C-5 and C-6), 118.79 (CN), 111.66 (C-1). Anal. Calcd for  $\text{C}_8\text{H}_7\text{N}_3$  (%): C, 66.19; H, 4.86. Found: C, 65.77; H, 4.82.

**Hydrazone of 4-bromophenylbenzaldehyde (1e).** The compound was obtained as colourless crystals, yield 72%, mp 77–78°C (from EtOH); IR (Nujol) ( $\nu$ ,  $\text{cm}^{-1}$ ): 1600 (C=N).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.66 (s, 1H, CH=N), 7.47 (d,  $^3J=8.6$  Hz, 2H, 3-H and 5-H), 7.39 (d,  $^3J=8.6$  Hz, 2H, 2-H and 6-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  141.48 (C=N), 134.07 (C-1), 131.66 (C-3 and C-5), 127.50 (C-2 and C-6), 122.43 (C-4). Anal. Calcd for  $\text{C}_7\text{H}_7\text{BrN}_2$  (%): C, 42.24; H, 3.54. Found: C, 42.45; H, 3.48.

**Hydrazone of 3-bromophenylbenzaldehyde (1f).** The compound was obtained as colourless crystals, yield 71%, mp 92–93°C (from EtOH); IR (Nujol) ( $\nu$ ,  $\text{cm}^{-1}$ ): 1635 (C=N).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.72 (dd,  $^4J=1.8$  Hz,  $^4J=1.8$  Hz, 1H, 2-H), 7.66 (s, 1H, CH=N), 7.45–7.40 (m, 2H, 4-H and 6-H), 7.21 (dd,  $^3J=7.9$  Hz,  $^3J=7.9$  Hz, 1H, 5-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  140.96 (C=N), 137.30 (C-1), 131.43, 130.11 and 128.88 (C-2, C-4 and C-5), 124.76 (C-6), 122.83 (C-3). Anal. Calcd for  $\text{C}_7\text{H}_7\text{BrN}_2$  (%): C, 42.24; H, 3.54. Found: C, 42.60; H, 3.21.

**Hydrazone of 4-chlorophenylbenzaldehyde (1g).** Yield 83%, mp 60–61°C (lit.<sup>15</sup> 57–58°C).

**Hydrazone of 3-chlorophenylbenzaldehyde (1h).** Yield 79%, mp 34–35°C (lit.<sup>16</sup> Bp 163–164°C/20).

**Hydrazone of 2-chlorophenylbenzaldehyde (1i).** Yield 74%, mp 60–61°C (lit.<sup>15</sup> 57–58°C).

**Hydrazone of 2,6-dichlorophenylbenzaldehyde (1k).** Yield 68%, mp 135°C (lit.<sup>9</sup> 134°C).

**Hydrazone of 2,4-dichlorophenylbenzaldehyde (1l).** Yield 78%, mp 83–84°C (lit.<sup>17</sup> 82–84°C).

**Hydrazone of benzaldehyde (1m).** Yield 89%,  $n_D^{20}$  1.6270 (lit.<sup>18</sup>  $n_D^{20}$  1.6271).

**Hydrazone of 4-dimethylaminophenylbenzaldehyde (1n).** Yield 82%, mp 69–72°C (lit.<sup>19</sup> 69–72°C).

**Hydrazone of 4-methoxyphenylbenzaldehyde (1o).** Yield 86%, mp 167–168°C (lit.<sup>20</sup> 166–167°C).

**2-Hydrazonomethyl-4-nitro-phenol (1p).** Yield 67%, mp 186–188°C (lit.<sup>21</sup> 186°C).

#### General procedure for dichlorostyrene preparation

A 25% aqueous solution of ammonia (3.33 ml) and  $\text{Cu}_2\text{Cl}_2$  (100 mg, 1 mmol) were added to a solution of hydrazone **1a–p** (10 mmol) in DMSO (10 ml). Then  $\text{CCl}_4$  (5 ml,

50 mmol) was added dropwise over 10 min, maintaining the temperature at 20°C. The reaction mixture was stirred for 4 h and quenched with water (300 ml); any aldazine **3a–p** that precipitated was filtered off. The reaction products were extracted with hexane (50 ml×3). The extracts were dried over sodium sulphate, hexane was evaporated and the residue was purified by column chromatography.

The known compounds **2a**, **2b**, **2c**, **2g**, **2h**, **2i**, **2k**, **2m**, **2n**, **2o**, **3a**, **3c**, **3e**, **3k**, **3m**, **3o** and **3p** were identified by comparison of the spectral data and melting point or boiling point with those described in the literature.

**1-(2,2-Dichlorovinyl)-4-nitrobenzene 2a.** Yield 79%, mp 94°C (lit.<sup>2</sup> 94°C).

**1-(2,2-Dichlorovinyl)-3-nitrobenzene 2b.** Yield 67%, mp 54°C (lit.<sup>6</sup> 53–55°C).

**4-(2,2-Dichlorovinyl)-benzoxazole 2c.** Yield 78%, mp 73–74°C (lit.<sup>6</sup> 75–76°C).

**3-(2,2-Dichlorovinyl)-benzoxazole 2d.** The compound was obtained as colourless crystals, yield 70%, mp 33–34°C (from EtOH); IR (Nujol) ( $\nu$ , cm<sup>-1</sup>): 2240 (CN), 1620 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.83 (dd, <sup>4</sup>J=1.8 Hz, <sup>4</sup>J=1.8 Hz, 1H, CH-2), 7.73 (ddd, <sup>3</sup>J=8.0 Hz, <sup>4</sup>J=1.8 Hz, <sup>4</sup>J=1.8 Hz, 1H, CH-6), 7.59 (ddd, <sup>3</sup>J<sub>HH</sub>=7.8 Hz, <sup>4</sup>J=1.5 Hz, <sup>4</sup>J=1.5 Hz, 1H, CH-4), 7.49 (dd, <sup>3</sup>J=8.0 Hz, <sup>3</sup>J=7.8 Hz, 1H, CH-5), 6.85 (s, 1H, Ar-CH=C). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  134.50 (C-1), 132.60 (C-2), 131.84 (C-6), 131.66 (C-4), 129.38 (C-5), 126.40 (C-1'), 123.85 (CCl<sub>2</sub>), 118.25 (CN), 112.84 (C-3). Anal. Calcd for C<sub>9</sub>H<sub>5</sub>Cl<sub>2</sub>N (%): C, 54.58; H, 2.54. Found: C, 54.38; H, 2.48.

**1-(2,2-Dichlorovinyl)-4-bromobenzene 2e.** The compound was obtained as colourless crystals, yield 57%, mp 24–25°C (from EtOH); IR (Nujol) ( $\nu$ , cm<sup>-1</sup>) 1620 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.45 (d, <sup>3</sup>J=8.6 Hz, 2H, CH-2,6), 7.35 (d, <sup>3</sup>J=8.6 Hz, 2H, CH-3,5), 6.74 (s, 1H, Ar-CH=C). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  132.12 (C-1), 131.59 (C-3,5), 130.04 (C-2,6), 127.41 (C-1'), 122.46 (C-4), 121.73 (CCl<sub>2</sub>). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>Cl<sub>2</sub>Br (%): C, 38.14; H, 2.00. Found: C, 38.42; H, 2.01.

**1-(2,2-Dichlorovinyl)-3-bromobenzene 2f.** The compound was obtained as colourless liquid, yield 66%,  $n_D^{17}$  1.6220. IR (Nujol) ( $\nu$ , cm<sup>-1</sup>) 1630 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H, CH-2), 7.40 (m, 2H, CH-4,6), 7.18 (dd, <sup>3</sup>J=8.0 Hz, <sup>3</sup>J=8.0 Hz, 1H, CH-5), 6.73 (s, 1H, Ar-CH=C). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  135.11 (C-1), 131.30 (C-6), 131.25 (C-4), 129.82 (C-5), 127.09 (C-1'), 127.06 (C-2), 122.44 (CCl<sub>2</sub>). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>Cl<sub>2</sub>Br (%): C, 38.14; H, 2.00. Found: C, 38.16; H, 1.96.

**1-(2,2-Dichlorovinyl)-4-chlorobenzene 2g.** Yield 74%,  $n_D^{20}$  1.5930 (lit.<sup>1</sup>  $n_D^{20}$  1.5914).

**1-(2,2-Dichlorovinyl)-3-chlorobenzene 2h.** Yield 65%, bp 103–105°C/1 Torr,  $n_D^{17}$  1.5970 (lit.<sup>6</sup> 103–105°C/1 Torr).

**1-(2,2-Dichlorovinyl)-2-chlorobenzene 2i.** Yield 64%,  $n_D^{20}$  1.5793 (lit.<sup>1</sup>  $n_D^{20}$  1.5793).

**1-(2,2-Dichlorovinyl)-2,6-dichlorobenzene 2k.** Yield 79%,  $n_D^{20}$  1.5850 (lit.<sup>2</sup>  $n_D^{20}$  1.5853).

**1-(2,2-Dichlorovinyl)-2,4-dichlorobenzene 2l.** The compound was obtained as colourless crystals, yield 62%, mp 49–50°C. IR (Nujol) ( $\nu$ , cm<sup>-1</sup>) 1620 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.65 (dd, <sup>3</sup>J=8.5 Hz, <sup>5</sup>J=0.6 Hz, 1H, CH-6), 7.43 (d, <sup>4</sup>J=2.1 Hz, 1H, CH-3), 7.28 (dd, <sup>3</sup>J=8.5 Hz, <sup>4</sup>J=2.1 Hz, 1H, CH-5), 6.99 (s, 1H, Ar-CH=C). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  134.80 (C-2), 134.21 (C-4), 130.78 (C-3), 130.44 (C-1), 129.39 (C-5), 127.02 (C-6), 124.70 (C-1'), 124.28 (CCl<sub>2</sub>). Anal. Calcd for C<sub>8</sub>H<sub>4</sub>Cl<sub>4</sub> (%): C, 39.72; H, 1.67. Found: C, 40.18; H, 1.56.

**1-(2,2-Dichlorovinyl)-benzene 2m.** Yield 27%,  $n_D^{20}$  1.5880 (lit.<sup>2</sup>  $n_D^{20}$  1.5874).

**4-(2,2-Dichlorovinyl)-N,N-dimethylaniline 2n.** Yield 26%, mp 70–71°C (lit.<sup>2</sup> mp 70–71°C).

**1-(2,2-Dichlorovinyl)-4-methoxybenzene 2o.** Yield 49%,  $n_D^{20}$  1.5978 (lit.<sup>6</sup>  $n_D^{20}$  1.5975).

**2-(2,2-Dichlorovinyl)-4-nitrophenol 2p** The compound was obtained as colourless crystals, yield 14%, mp 153–155°C. IR (Nujol) ( $\nu$ , cm<sup>-1</sup>) 1630 (C=C), 1530 (NO<sub>2</sub>), 1380 (O–H). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  10.96 (s, 1H, OH), 8.62 (d, <sup>4</sup>J=2.8 Hz, 1H, CH-3), 8.04 (dd, <sup>3</sup>J=9.0 Hz, <sup>4</sup>J=2.8 Hz, 1H, CH-5), 7.09 (s, 1H, CH), 7.01 (d, 1H, CH-6, <sup>3</sup>J=9.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  160.47 (C-1), 139.12 (C-4), 124.76 (C-1'), 124.20 (C-5), 121.78 (C-3), 121.62 (CCl<sub>2</sub>), 120.15 (C-2), 114.92 (C-6). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>Cl<sub>2</sub>NO<sub>3</sub> (%): C, 41.06; H, 2.15. Found: C, 41.32; H, 2.30.

**4-Nitrobenzaldehyde (4-nitrobenzylidene)hydrazone 3a.** Yield 17%, mp 296–297°C (lit.<sup>22</sup> 296–297°C).

**4-Formylbenzoxazole (4-cyanobenzylidene)hydrazone 3c.** Yield 17%, mp 318–320°C (lit.<sup>23</sup> 296–297°C).

**4-Bromobenzaldehyde (4-bromobenzylidene)hydrazone 3e.** Yield 40%, mp 222–224°C (lit.<sup>24</sup> 223.5–224.5°C).

**2,6-Dichlorobenzaldehyde (2,6-dichlorobenzylidene)hydrazone 3k.** Yield 15%, mp 152–153°C (lit.<sup>25</sup> 153°C).

**Benzaldehyde (benzylidene)hydrazone 3m.** Yield 68%, mp 92–93°C (lit.<sup>26</sup> 93–94°C).

**4-Methoxybenzaldehyde (4-methoxybenzylidene)hydrazone 3o.** Yield 44%, 167–168°C (lit.<sup>27</sup> 168–169°C).

**2-Hydroxy-5-nitro-benzaldehyde (2-hydroxy-5-nitrobenzylidene)hydrazone 3p.** Yield 80%, mp 298°C (lit.<sup>21</sup> 300°C).

#### Acknowledgements

Financial support from the Russian Foundation for Basic Research (Grant No. 00-03-32760a) is gratefully acknowledged.

## References

1. Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1975**, 458.
2. Speziale, A. J.; Ratts, K. W. *J. Am. Chem. Soc.* **1962**, *84*, 854.
3. Seyferth, D.; Marmor, R. S. *J. Organomet. Chem.* **1973**, *59*, 237.
4. Gajewski, R. P.; Jackson, J. L.; Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B. *J. Org. Chem.* **1989**, *54*, 3311.
5. Tanaka, H.; Yamashita, S.; Yamanoue, M.; Torii, S. *J. Org. Chem.* **1989**, *54*, 444.
6. Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 1305.
7. Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova, E. S. *Russ. Chem. Bull.* **1999**, *48*, 2184.
8. Reichardt, C. *70. Solvent Effects in Organic Chemistry*; Chemie Weinheim: New York, 1979; pp 270–272.
9. Lock, G.; Stach, K. *Chem. Ber.* **1943**, *76*, 1252.
10. Assher, M.; Vofsi, D. *J. Chem. Soc. (B)* **1968**, 947.
11. Houben-Weil *In Methoden der Organischen Chemie*; Georg Thieme: Stuttgart, 1968; Vol. 10/4, pp 567–577.
12. Reimlinger, H. *Chem. Ber.* **1964**, *97*, 339.
13. Curtius, T.; Lublin, A. *Chem. Ber.* **1900**, *33*, 2464.
14. Hinman, R. L. *J. Org. Chem.* **1960**, *25*, 1775.
15. Singh, G.; Zimmer, H. *J. Org. Chem.* **1965**, *30*, 417.
16. Curtius, T.; Franzen, H. *Chem. Ber.* **1902**, *35*, 3238.
17. Werbel, L. M.; Hung, J.; McNamara, D.; Ortwine, D. F. *Eur. J. Med. Chem. Chim. Ther.* **1985**, *20*, 363.
18. Kline, G. B.; Cox, S. H. *J. Org. Chem.* **1961**, *26*, 1854.
19. Shirinian, V. Z.; Belen'kii, L. I.; Krayushkin, M. M. *Russ. Chem. Bull.* **1999**, *48*, 2171.
20. Franzen, H.; Eichler, T. *J. Prakt. Chem.* **1910**, *82*, 241.
21. Jain, M. P.; Kumar, S. *Talanta* **1979**, *26*, 909.
22. Tsuge, O.; Kanemasa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3591.
23. Barber, H. J.; Slack, R. *J. Am. Chem. Soc.* **1943**, *65*, 1776.
24. Ferguson, L. N.; Goodwin, T. C. *J. Am. Chem. Soc.* **1949**, *71*, 633.
25. Mobbs, D. B.; Suschitzky, H. *Tetrahedron Lett.* **1971**, 361.
26. Rosini, G.; Soverini, M.; Ballini, R. *Synthesis* **1983**, *11*, 909.
27. Chattopadhyaya, J. B.; Rao, A. V. R. *Indian J. Chem.* **1975**, *13*, 632.