



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

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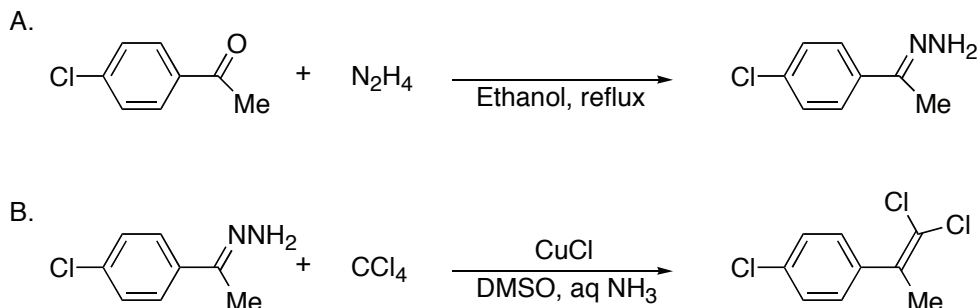
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions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

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**CONVERSION OF ARYLALKYLKETONES INTO  
DICHLOROALKENES:  
1-CHLORO-4-(2,2-DICHLORO-1-METHYLVINYLBENZENE  
(1-Chloro-4-(2,2-dichloro-1-methylethenyl)-benzene)**



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Checked by Kristin Brinner and Jonathan A. Ellman.

### 1. Procedure

*A. 1-(4-Chlorophenyl)ethanone hydrazone.* A single-necked, 250-mL round-bottomed flask equipped with a reflux condenser is charged with absolute ethanol (100 mL) (Note 1), 100% hydrazine hydrate (9.7 mL, 0.2 mol) (Note 2) and 1-(4-chlorophenyl)ethanone (13.0 mL, 0.1 mol) (Note 3). The reaction solution is refluxed for 3 h. The ethanol and excess of hydrazine are removed by evaporation at ca. 50 °C/20 mm (Note 4). The slight-yellow crude 1-(4-chlorophenyl)ethanone hydrazone is redissolved in 10 mL of hot ethanol (Note 1). The mixture is cooled to –18 °C, kept at that temperature overnight and filtered. The solid is washed with hexane (2 x 20 mL) (Note 5) and dried under vacuum (2-3 mm) for 2 h to afford 13.6-14.8 g (81-88%) of colorless crystals (Note 6). The product is stored at –18 °C until used in step B (Note 7).

*B. 1-Chloro-4-(2,2-dichloro-1-methylvinyl)benzene.* A single-necked, 250 mL round-bottomed flask equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel is charged with dimethyl sulfoxide (DMSO) (50 mL) (Note 8), 1-(4-chlorophenyl)ethanone hydrazone (8.4 g, 0.05 mol) (Note 6) and 28% aqueous ammonium hydroxide (16.8 mL, 0.25 mol) (Note 9). Freshly purified copper (I) chloride (500 mg, 0.005 mol)

(Note 10) was added in one portion. After 5 min, carbon tetrachloride (24 mL, 0.25 mol) (Note 11) is added dropwise over 30 min (Note 12), while the temperature is maintained between 15-20 °C (water bath). After the addition is complete, the reaction mixture is stirred at room temperature overnight and quenched with 500 mL of 5% aqueous hydrochloric acid. The reaction products are extracted with hexane (4 x 50 mL) (Note 5). The combined extracts are dried over anhydrous sodium sulfate. After filtration and removal of the solvent by rotary evaporation (Note 13), the yellow crude product is purified by flash chromatography (5.0 x 5.0 cm) through silica gel (30 g, 63-200 mesh) using hexane (4-5 50 mL portions) (Notes 13 and 14) to afford 8.64-8.85 g (78-80% yield) of 1-chloro-4-(2,2-dichloro-1-methylvinyl)benzene as a colorless viscous oil that is > 98% pure by <sup>1</sup>H NMR analysis (Note 15).

## 2. Notes

1. Reagent grade ethanol was used without further purification by the checkers.
2. 100% Hydrazine hydrate was purchased from E. Merck.
3. 1-(4-Chlorophenyl)ethanone (98% purity) was purchased from E. Merck. The checkers purchased 97% purity material from Aldrich.
4. The checkers report that ethanol was removed by rotary evaporation at 30 mm with the bath temperature at 30 °C. Hydrazine was then removed at 10 mm with the bath temperature at 25 °C. The submitters report that the ethanol-hydrazine mixture collected in a trapping flask can be used for the preparation of next portion of hydrazone.
5. Reagent grade hexane was used without further purification.
6. mp 48.4-50.1 °C (the same melting point was observed after repeated recrystallizations; however, the submitters report a mp of 55-56 °C). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 2.00 (s, 3H), 6.46 (s, 2H), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.8, 2H), 7.61 (d, <sup>3</sup>J<sub>HH</sub> = 8.8, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 11.1, 126.7, 128.4, 131.9, 139.2, 141.1. IR (nujol) cm<sup>-1</sup>: 3365, 3310, 3225, 2970, 2945, 2865, 1640, 1600, 1490, 1430, 1380, 1285, 1135, 1100, 1070, 1015, 970, 840. <sup>3</sup>
7. The submitters do not recommend the use of hydrazone stored more than 7 days as this results in decreased yields.

8. Reagent grade DMSO (99.6% purity) purchased from Sigma Aldrich was used without further purification.

9. Ammonium hydroxide (28% NH<sub>3</sub> in water) was purchased from the Sigma-Aldrich Company.

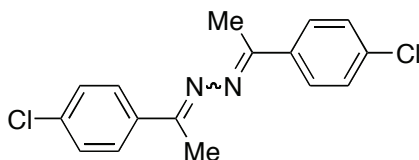
10. Commercially available copper (I) chloride (98% purity) purchased from Sigma-Aldrich (10 g) was dissolved in 100 mL of 10% HCl, precipitated by dilution with 1000 mL of water and filtered. The solid was washed with water (100 mL), ethanol (100 mL), acetone (100 mL) and ethyl ether (100 mL), and then dried under vacuum (2-3 mm) in a desiccator.

11. Reagent grade CCl<sub>4</sub> (99.5% purity) purchased from Sigma-Aldrich was used without further purification.

12. Intense gas evolution is observed. A characteristic color change from slight-green to blue occurs.

13. Care should be taken to keep the bath temperature at 25 °C during rotary evaporation of hexanes because the product is moderately volatile.

14. The main impurity (TLC (hexane:CH<sub>2</sub>Cl<sub>2</sub>; 2:1): R<sub>f</sub> 0.45) was identified as the azine of 1-(4-chlorophenyl)ethanone.



15. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.17 (s, 3H), 7.19 (d, <sup>3</sup>J<sub>HH</sub> = 8.8, 2H), 7.32 (d, <sup>3</sup>J<sub>HH</sub> = 8.8, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 22.9, 117.6, 128.6, 129.2, 133.6, 134.5, 138.4. IR (neat) cm<sup>-1</sup>: 2930, 2860, 1915, 1650, 1615, 1595, 1490, 1430, 1400, 1380, 1265, 1100, 1070, 1040, 1020, 920, 840. TLC (R<sub>f</sub> (hexane) 0.55). Found: C, 49.02; H, 3.14. Calcd for C<sub>9</sub>H<sub>7</sub>Cl<sub>3</sub>: C, 48.80; H, 3.18 %.

### Safety and Waste Disposal Information

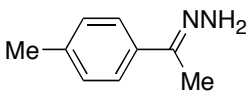
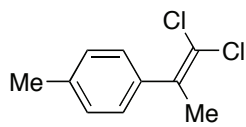
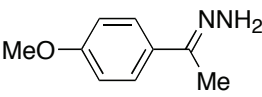
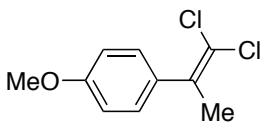
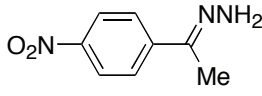
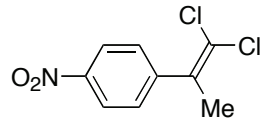
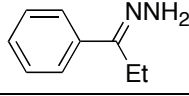
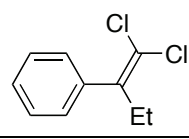
All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

### 3. Discussion

Development of new catalytic methods for the construction of double carbon-carbon bonds is a goal of modern synthetic chemistry. Olefination of carbonyl compounds, that is, conversion of the carbonyl group into C=C fragment, is a widely used approach for the formation of alkenes. Wittig-type reactions, Peterson and Julia olefination and reductive couplings of carbonyl compounds are the most common olefination methods.<sup>4,5</sup> However, the necessity to use equimolar quantities or a large excess of phosphorus, silicon, sulfur reagents or metals is a significant disadvantage of these techniques.

Table 1

Preparation of Dichloroalkenes

Substrate	Product	Yield
		65
		70
		58
		57

The present procedure describes a convenient preparation of dichloroalkenes from aryl alkyl ketones based on a novel catalytic olefination reaction (COR) of carbonyl compounds.<sup>6</sup> Some representative examples of dichloromethylenation of ketones are compiled in Table 1.

Recently we found that *N*-unsubstituted hydrazones of aldehydes and ketones could be transformed into alkenes when treated with polyhalogenated alkanes in the presence of copper (I) chloride. This method has already found applications in the synthesis of dihaloalkenes,<sup>6</sup> monohaloalkenes,<sup>7</sup> fluorinated olefins,<sup>8</sup> and a range of alkenes containing functional groups<sup>9</sup> from the corresponding carbonyl precursors (Figure 1).

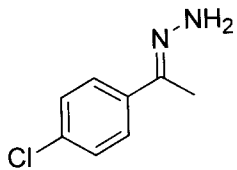


6. (a) Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2000**, *56*, 6557; (b) Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova, E. S. *Synthesis* **2001**, 2081; (c) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *J. Chem. Soc. Perkin Trans. 1* **2002**, 883; (d) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *Org. Biomol. Chem.* **2003**, *1*, 1906.
7. (a) Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova, E. S. *Russ. Chem. Bull.* **2001**, *50*, 1401; (b) Shastin, A. V.; Korotchenko, V. N.; Varseev G. N.; Nenajdenko, V. G.; Balenkova, E. S. *Russ. J. Org. Chem.* **2003**, *39*, 403.
8. (a) Korotchenko, V. N.; Shastin, A. V.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2001**, *57*, 7519; (b) Nenajdenko, V. G.; Shastin, A. V.; Korotchenko, V. N.; Varseev G. N.; Balenkova, E. S. *Eur. J. Org. Chem.* **2003**, 302; (c) Nenajdenko, V. G.; Varseev G. N.; Korotchenko, V. N.; Shastin, A. V.; Balenkova, E. S. *J. Fluorine Chem.* **2003**, *124*, 115.
9. (a) Nenajdenko, V. G.; Lenkova O. N.; Shastin, A. V.; Balenkova, E. S. *Synthesis* **2004**, 573; (b) Nenajdenko, V. G.; Shastin, A. V.; Golubinskii I. V.; Lenkova O. N.; Balenkova, E. S. *Russ. Chem. Bull.* **2004**, *1*, 218.

### Appendix

#### Chemical Abstracts Nomenclature (Registry Number)

Hydrazine hydrate: Hydrazine, monohydrate; (7803-57-8)  
1-(4-Chlorophenyl)ethanone; (99-91-2)  
1-(4-Chlorophenyl)ethanone hydrazone; (40137-41-5)  
Copper (I) chloride: Copper chloride; (7758-89-6)  
Carbon tetrachloride: Tetrachloromethane; (56-23-5)



(500 MHz, DMSO- $d_6$ )

7.620  
7.615  
7.611  
7.601  
7.597  
7.592  
7.347  
7.342  
7.338  
7.328  
7.324  
7.319  
6.460

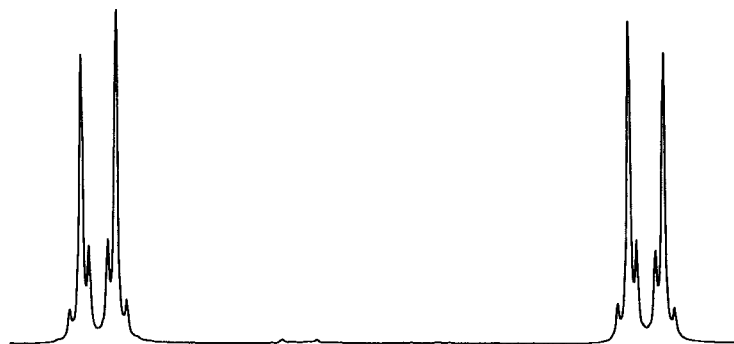
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7.615  
7.611  
7.601  
7.597  
7.592

3.327

7.347  
7.342  
7.338  
7.328  
7.324  
7.319

2.489  
2.485  
2.482

1.986



7.60 7.55 7.50 7.45 7.40 7.35 ppm

9 8 7 6 5 4 3 2 1 ppm

1.97

1.92

2.01

0.27

0.30

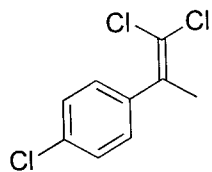
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3.00

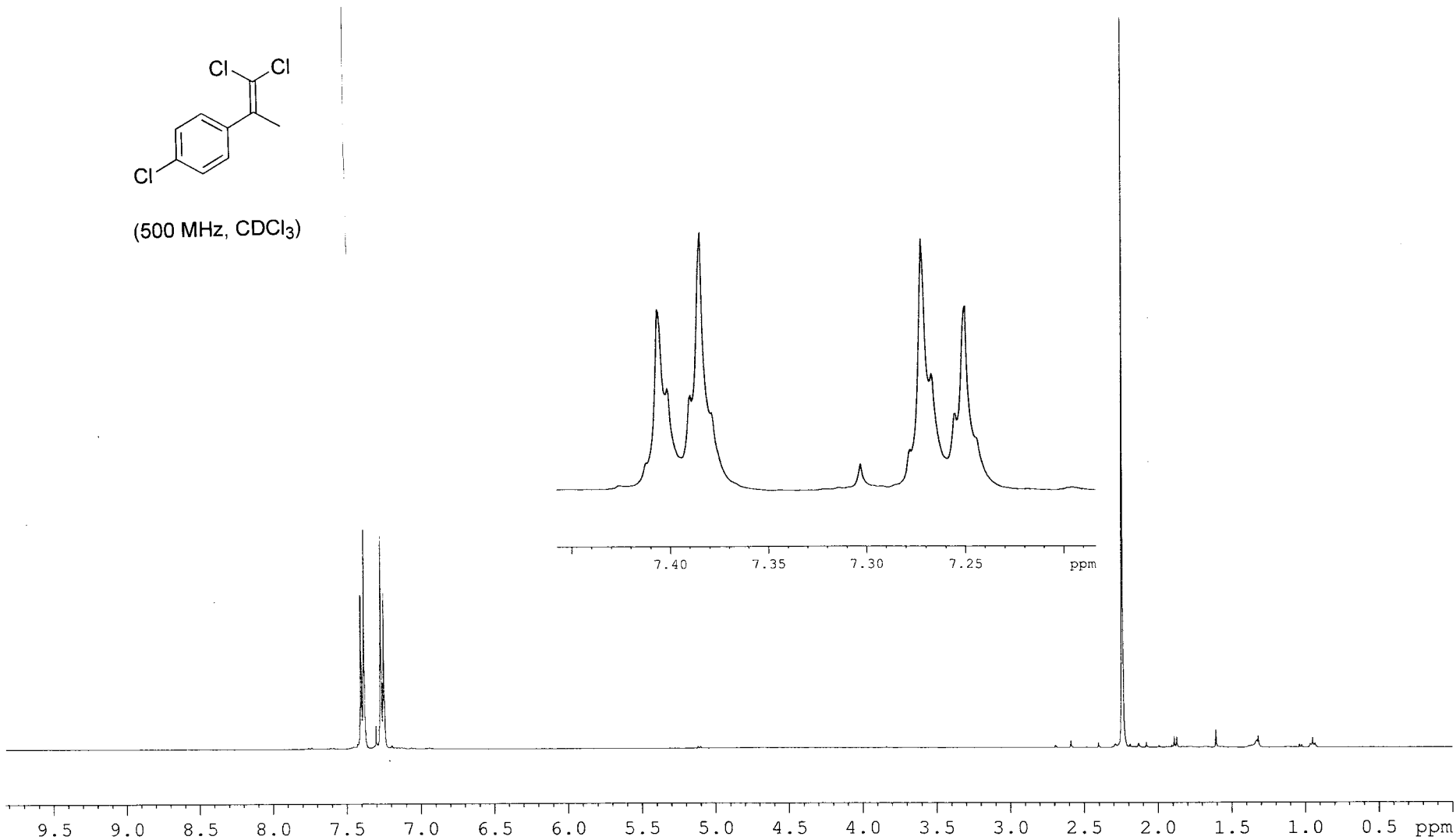


7.760  
7.738  
7.609  
7.589  
7.449  
7.426  
7.412  
7.406  
7.402  
7.390  
7.385  
7.379  
7.314  
7.303  
7.278  
7.272  
7.267  
7.255  
7.250  
7.218  
7.196  
7.172  
7.152  
7.136  
7.114  
7.066  
7.050  
7.044  
6.970  
6.943  
6.922  
5.138  
5.120  
5.104  
5.086

3.839  
2.692  
2.589  
2.481  
2.402  
2.288  
2.242  
2.189  
2.131  
2.078  
1.993  
1.907  
1.892  
1.875  
1.836  
1.784  
1.677  
1.607  
1.574  
1.488  
1.385  
1.368  
1.332  
1.321  
1.122  
1.076  
1.041



(500 MHz, CDCl<sub>3</sub>)



2.00  
1.90

2.89  
0.08  
0.06  
0.18  
0.10