Letters to the Editor

A novel reaction of double carbon—carbon bond formation: synthesis of 2,2-dichlorostyrenes

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Currently, metal complex catalysis is one of the most intensely developing fields of organic chemistry. Great attention is devoted to the oxidation of a wide range of organic compounds by oxygen in the presence of copper-containing systems.¹ However, examples of using other oxidants in the presence of copper compounds are rather rare.² Polyhaloalkanes (most often, carbon tetrachloride) can act as such oxidants.^{3–8}

We found a novel redox reaction of double carboncarbon bond formation catalyzed by copper salts, which permits the preparation of 2,2-dichlorostyrenes from *N*-unsubstituted hydrazones of aromatic aldehydes.



 $\label{eq:Ar} \text{Ar} \ = \ 4\text{-}\text{NO}_2\text{C}_6\text{H}_4 \ (\textbf{a}), \ \text{C}_6\text{H}_5 \ (\textbf{b}), \ 4\text{-}\text{MeOC}_6\text{H}_4 \ (\textbf{c}).$

This reaction proceeds in a DMSO solution in the presence of a base (an aqueous solution of ammonia). The treatment of hydrazones in the presence of a catalytic amount of copper monochloride results in the formation of the corresponding dichlorostyrenes, which are valuable intermediates for organic synthesis and can be used for the preparation of terminal acetylenes and chloroacetylenes.^{9,10}

The yield of dichlorostyrenes depends on the nature of the substituent in the aromatic ring and decreases in the series 2a > 2c > 2b (79, 49, and 27%, respectively).

The corresponding azines (3a-c) are formed along with dichlorostyrenes in the reaction mixture, and the overall yield of products 2 and 3 is close to quantitative. All compounds synthesized were characterized by the set of ¹H and ¹³C NMR spectroscopic data and by comparison of their parameters with those reported in the literature.

Further we are planning to study the factors that affect the course of the reaction and the yield of target products (the nature and amount of catalysts, the ratio of the reagents, and the nature of the solvent) as well as a possible mechanism of the reaction.

Synthesis of dichlorostyrenes 2a--c (general procedure). A 25% aqueous solution of ammonia (3.33 mL) and Cu_2Cl_2 (100 mg, 1 mmol) were added to a solution of hydrazone 1 (10 mmol) in DMSO (10 mL). Then CCl₄ (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

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with a 0.1 M solution of hydrochloric acid (300 mL). The reaction products were extracted with hexane (50 mL \times 3), and aldazine 3 that precipitated was filtered off. The extracts were dried over sodium sulfate, hexane was evaporated, and the residue was purified by column chromatography. The spectral parameters of compounds 2a-c correspond to those reported in the literature.

1-(2,2-Dichloroviny!)-4-nitrobenzene (2a), yield 79%, m.p. 94 °C (Ref. 10: m.p. 94 °C).

1-(2,2-Dichlorovinyl)benzene (2b), yield 27%, n_D^{20} 1.5880 (Ref. 10: n_D^{20} 1.5874).

1-(2,2-Dichlorovinyl)-4-methoxybenzene (2c), yield 49%, n_D^{20} 1.5978 (Ref. 9: n_D^{20} 1.5975).

4-Nitrobenzaldehyde (4-nitrobenzylidene)hydrazone (3a), yield 17%, m.p. 296-297 °C (Ref. 11: m.p. 296-297 °C).

Benzaldehyde benzylidenehydrazone (benzalazine) (3b), yield 68%, m.p. 92-93 °C (Ref. 12: m.p. 92-93 °C).

4-Methoxybenzaldehyde (4-methoxybenzylidene)hydrazone (3c), yield 44%, m.p. 167-168 °C (Ref. 13: m.p. 168-169 °C).

Starting hydrazones 1a-c were synthesized by the previously described procedure.¹⁴

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