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LETTERS TO THE EDITOR

Chlorobromination of Phenylacetylene with the $SnCl_4$–Br_2 System

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2-Bromo-1-chloro-1-phenylethene can be synthesized by chlorination of bromoethynylbenzene with sodium chloride in dimethyl sulfoxide [1], chlorination of bromomethyl phenyl ketone with phosphorus(V) chloride [1], conjugate halogenation of phenylacetylene with bromine in the presence of copper chloride [2], replacement of the bromine atom in the α-position of (1,2-dibromovinyl)benzene by the action of $SbCl_5$ in CCl_4 [2], reaction of phenylacetylene with bromine chloride or tetrabutylammonium dichlorobromate [3], and treatment of phenylacetylene with Amberlyte A-26 ion exchanger in the dichlorobromate form ($BrCl_2^-$) [4]. 1-Bromo-2-chloro1-phenylethene was synthesized by bromination 1-chloro-2-phenylacetylene with KBr in DMSO [1], and (2,2-dibromovinyl)benzene was prepared by decomposition of phenyl 1,2-dibromo-1-chloro-2-phenylethyl ketone with sodium methoxide in methanol [5] or by condensation of benzaldehyde with bromotrichloromethane in the presence of zinc and triphenylphosphine [1].

We have discovered a new and convenient chlorobrominating system consisting of tin(IV) chloride and molecular bromine at a ratio of 1:1. Treatment of phenylacetylene with that system gives mainly the corresponding chlorobromination product, 2-bromo-1-chloro-1-phenylethene (**I**).

$$C_6H_5C{\equiv}CH \xrightarrow[CCl_4]{SnCl_4–Br_2} \underset{\mathbf{I}}{Z,E\text{-}C_6H_5CCl{=}CHBr}.$$

We succeeded in attaining 87% selectivity in this reaction, and the yield of vinylbenzene **I** was 73%. The reaction is accompanied by formation of 11% of 1,2-dibromo-1-phenylethene **II** as by-product. Presumably, the process involves formation of bromine chloride via exchange of chlorine in $SnCl_4$ for bromine.

The regioselectivity in the chlorobromination of phenylacetylene was determined by dehydrohalogenation of the product mixture (**I** and **II**), which led to formation of 1-bromo-2-phenylacetylene $C_6H_5C{\equiv}CBr$. The absence of chloroethynylbenzene among the dehydrohalogenation products unambiguously indicates formation of 2-bromo-1-chloro-1-phenylethene (**I**). The addition of bromine at the terminal carbon atom of phenylacetylene also follows from comparison of the ^{1}H NMR spectra of the chlorobromination products with the calculated and publiched values for different regio- and stereoisomers [1, 2, 6]. According to the ^{1}H NMR data, compound **I** is formed mainly as *trans* isomer.

^{1}H NMR and gas chromatogrphic–mass spectrometric studies showed that the time of preliminary contact of bromine with tin(IV) chloride affects the reaction selectivity and that the temperature affects the stereochemistry of the process, for *E* isomer *E*-**I** is a kinetically controlled product which undergoes transformation into thermodynamically more stable isomer *Z*-**I**. In the temperature range from –20 to 0°C, the ratio *E*-**I**:*Z*-**I** is (2.6–3):1, while at 20°C it changes to (1.2–1.4):1. Heating of a mixture containing mainly the trans isomer (*E*:*Z* = 1.4:1) leads to considerable increase in the fraction of the *cis* isomer (*E*:*Z* = 1:7, 120°C, 1 h).

The reaction mixtures obtained by preliminarily heating $SnCl_4$ with Br_2 for a short time (5–20 min) contained 1,2-dibromo-1,2-dichloroethylbenzene (**III**) and 2-bromo-1,1-dichloroethylbenzene (**IV**) (according to the ^{1}H NMR and GC–MS data). Compound **III** is formed by further chlorobromination of **I**, while compound **IV** is the hydrochlorination product of **I**. In the ^{1}H NMR spectrum of **III**, the CHClBr proton gives a singlet at δ 6.21 ppm. The mass spectrum of **III** contains the molecular ion peak $[M]^{+\cdot}$ with *m/z* 332 (35Cl, 80Br), and peaks from fragment ions $[PhC{\equiv}CBr]^+$ (*m/z* 181), $[PhCCl{=}CH]^+$ (137), and $[PhC{\equiv}CH]^{+\cdot}$ (102). Ethylbenzene **IV** showed in the

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^{1}H NMR spectrum a singlet at δ 4.29 ppm from the CH_2Br group, and its mass spectrum contained the molecular ion peak $[M]^{+\cdot}$ with *m/z* 252 (^{35}Cl, ^{80}Br) and fragment ion peak $[PhCCl_2]^+$ with *m/z* 159.

Although the overall concentration of the *Z* and *E* isomers of **I** obtained at low temperature is lower than in the reaction performed at room temperature, the overall yield in the chlorobromination of phenylacetylene (with account taken of compounds **III** and **IV**) is generally constant and is 80–87%.

Reaction of phenylacetylene with $SnCl_4$–Br_2. A mixture of 4.28 g of bromine and 7.03 g of tin(IV) chloride in 20 ml of carbon tetrachloride was stirred for 8 h at 20°C, 2.76 g of phenylacetylene was added, and the mixture was stirred for 4.5 h. It was then treated with a saturated solution of $Na_2S_2O_3$, the organic phase was separated and dried over $CaCl_2$, and the solvent was removed to obtain 4.97 g of a mixture of isomers *Z,E*-**I** and *Z,E*-**II**, which contained (according to the ^{1}H NMR data), 87% of **I** (yield 73%). ^{1}H NMR spectrum, δ, ppm: 7.30–7.37 m, 7.49–7.51 m, 7.53–7.56 m (C_6H_5); 6.83 s (1H, =CHBr, *Z*-**I**); 6.58 s (1H, =CHBr, *E*-**I**); 7.01 s (1H, =CHBr, *Z*-**II**); 6.76 s (1H, =CHBr, *E*-**II**). Published data: 6.81 s (*Z*-**I**) [1, 2], 6.50 s (*E*-**I**) [1], 6.55 s (*E*-**I**) [2], 7.00 s (*Z*-**II**) [6], 6.75 s (*E*-**II**) [6]. Mass spectrum, *m/z*: **I**: 220, 218, 216 $[M]^{+\cdot}$; 181 $[M - Cl]^+$; 137 $[M - Br]^+$, 102 $[PhC{\equiv}CH]^{+\cdot}$; **II**: 264, 262,260 $[M]^{+\cdot}$; 183 $[M - Br]^+$; 137 $[M - 2\ Br]^+$; 102 $[PhC{\equiv}CH]^{+\cdot}$.

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker DPX-400 spectrometer (400 MHz). The GC–MS data were acquired on a Hewlett–Packard HP-5971A mass-selective detector (electron impact, 70 eV).

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