

SHORT  
COMMUNICATIONS

## Iodosobenzene Dichloride, a Convenient Reagent for Chloro- and Iodomethoxylation of Double and Triple Bonds\*

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Iodosobenzene dichloride (**I**), an organic compound of polyvalent iodine, is extensively used in organic synthesis for chlorination and oxidation of a wide range of compounds [1-3]. However published reports on application of the compound to haloalkoxylation are lacking.

We established that the reaction of  $\text{PhICl}_2$  with styrene derivatives **II-IV** in methanol at room temperature easily gave rise to products of electrophilic chloromethoxylation **V-VII** in 68-90% yield.

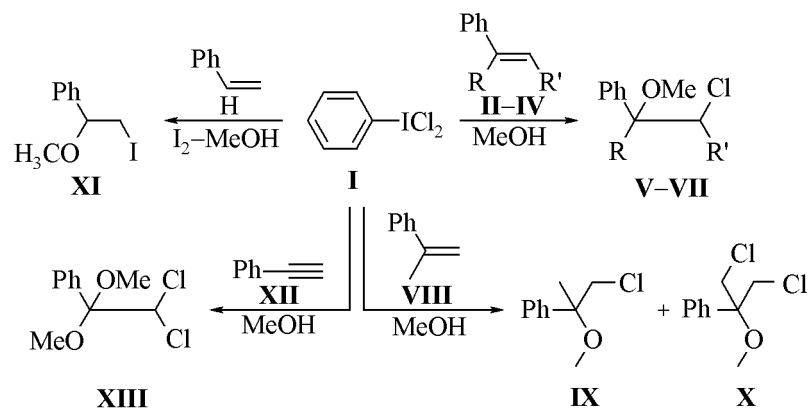
The chloromethoxylation proceeded as a typical electrophilic addition, and therewith, as was shown by an example of *trans*-stilbene (**III**), occurred predominantly *anti*-addition to furnish *erythro*-diastereomer **VI** in 64% yield (the yield of *threo*-isomer **VI** was 36%).

The reaction with  $\alpha$ -methylstyrene (**VIII**) was less selective and afforded in 70% overall yield an inseparable mixture of two isomers **IX** and **X** in 75:25 ratio according to GC-MS and <sup>1</sup>H NMR data. The

formation of reaction product **X** is an evidence of a contribution from free-radical chlorination of the methyl group in compound **IX** [or in initial  $\alpha$ -methylstyrene (**VIII**)] effected by  $\text{PhICl}_2$ .

It turned out that reaction of styrene (**II**) with  $\text{PhICl}_2$  in methanol in the presence of iodine took another route easily providing a product of iodomethoxylation of the double bond **XI** in 80% yield. Obviously here the iodosobenzene dichloride acted as oxidant for iodine providing its electrophilic intermediates ( $\text{I}^+$ ,  $\text{ICl}$ , or  $\text{CH}_3\text{OI}$ ). This reaction is perhaps the first example of a simple iodoalkoxylation of alkenes with the use of compounds of polyvalent iodine, and it opens new opportunities for the synthesis of commonly less available iodoalkoxyalkanes [4, 5].

Phenylacetylene (**XII**) reacted with two moles of compound **I** in methanol furnishing 1,1-dimethoxy-1-phenyl-2,2-dichloroethane (**XIII**) in 65% yield. Compound **XIII** was formerly prepared by reaction of



$\text{R} = \text{R}' = \text{H}$  (**II**, **V**);  $\text{R} = \text{R}' = \text{Ph}$  (**III**, **VI**);  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{H}$  (**IV**, **VII**).

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phenylacetylene with chlorine or *N*-chlorosuccinimide in methanol (yield 70–81%) [6].

Thus iodosobenzene dichloride provides a possibility to perform both chloro- and iodomethoxylation of aromatic alkenes and alkynes under mild conditions.

**General procedure of the synthesis.** To a solution of 2.0 mmol of alkene in 8.0 ml of MeOH was added 2.02 mmol of iodosobenzene dichloride (**I**), and the mixture was stirred at room temperature for 20 min. The mixture was poured into 30 ml of water, extracted with ether (2×30 ml), the extract was washed with water (2×50 ml), with saturated NaCl solution (50 ml), and dried on Na<sub>2</sub>SO<sub>4</sub>. On removing the ether the residue was dissolved in benzene (2 ml) and applied to a column packed with silica gel. Elution with hexane afforded 390 mg of iodobenzene (95%) (bp 188°C [7]). The reaction products **V**, **VII**, **XIII** were eluted with hexane–benzene, 4:1.

**1-Methoxy-1-phenyl-2-chloroethane (V).** Yield 68%, oily substance, bp 82–85°C/hexane–benzene mixture, 4:1. 6 mm Hg (publ. bp 79–82°C/4 mm Hg [8]). <sup>1</sup>H NMR spectrum (500 MHz, CCl<sub>4</sub>-CDCl<sub>3</sub>, 3:1, δ, ppm, *J*, Hz): 3.27 s (3H, OCH<sub>3</sub>), 3.50 d.d (1H, CH<sub>a</sub>, *J* 4.5, 11.5), 3.60 d.d (1H, CH<sub>b</sub>, *J* 7.5, 11.5), 4.27 d.d (1H, *J* 4.5, 7.5), 7.26–7.34 m (5H arom). <sup>13</sup>C NMR spectrum (500 MHz, CCl<sub>4</sub>-CDCl<sub>3</sub>, 3:1, δ, ppm): 47.80 (CH<sub>2</sub>), 56.99 (OCH<sub>3</sub>), 83.79 (CH), 126.76, 128.35, 128.50, 138.72 (C arom). Found, %: C 63.40; H 6.43; Cl 20.04. C<sub>11</sub>H<sub>11</sub>ClO. Calculated, %: C 63.35; H 6.50; Cl 20.78.

**1-Methoxy-1,2-diphenyl-2-chloroethane (VI).** Yield 90%. *erythro*-(**VI**) mp 98–100°C (publ. mp 95–97°C [8]). <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, δ, ppm, *J*, Hz): 3.18 s (3H, OCH<sub>3</sub>), 4.53 d (1H, *J* 7.0), 4.97 d (1H, *J* 7.0), 7.24–7.29 m (10H arom). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 57.35 (OCH<sub>3</sub>), 65.32 (CHCl), 87.14 (CHOCH<sub>3</sub>), 127.89, 127.95, 128.24, 128.14, 137.71, 138.22 (C arom). Found, %: C 73.05; H 6.24; Cl 13.97. C<sub>15</sub>H<sub>15</sub>ClO. Calculated, %: C 73.02; H 6.13; Cl 14.37. *threo*-(**VI**) oily substance (publ. oily substance [8]). <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, δ, ppm, *J*, Hz): 3.31 s (3H, OCH<sub>3</sub>), 4.46 d (1H, *J* 8.0), 4.95 d (1H, *J* 8.0), 7.17–7.22 m (10H arom). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 57.21 (OCH<sub>3</sub>), 66.75 (CHCl), 87.66 (CHOCH<sub>3</sub>), 127.58, 127.94, 127.99, 128.21, 137.47, 138.15 (C arom). Found, %: C 73.27; H 6.37; Cl 13.90. C<sub>15</sub>H<sub>15</sub>ClO. Calculated, %: C 73.02; H 6.13; Cl 14.37.

**1-Methoxy-1,1-diphenyl-2-chloroethane (VII).** Yield 72%, mp 47–49°C (publ. oily substance [8]). <sup>1</sup>H NMR spectrum (CCl<sub>4</sub>-CDCl<sub>3</sub>, 3:1, δ, ppm): 3.12 s (3H, OCH<sub>3</sub>), 4.22 s (2H), 7.19 t (4H arom) 7.22 t (6H arom), 7.30 (4H arom). <sup>13</sup>C NMR spectrum (CCl<sub>4</sub>-CDCl<sub>3</sub>, 3:1, δ, ppm): 48.36 (CH<sub>2</sub>Cl), 50.57 (OCH<sub>3</sub>), 81.69 (COCH<sub>3</sub>), 127.14, 127.30, 128.05, 142.43 (C arom). Found, %: C 72.96; H 6.47; Cl 13.70. C<sub>15</sub>H<sub>15</sub>ClO. Calculated, %: C 73.02; H 6.13; Cl 14.37.

**1,1-Dimethoxy-1-phenyl-2,2-dichloroethane (XIII).** Yield 65%, mp 68–69°C (publ. mp 66–67.5°C [6]). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 3.34 s (6H, OCH<sub>3</sub>), 5.97 s (1H), 7.39 m (3H arom) 7.62 m (2H arom). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 49.89 (OCH<sub>3</sub>), 73.10 (CCl<sub>2</sub>), 102.81 [C(OCH<sub>3</sub>)<sub>2</sub>], 127.86, 128.89, 129.22, 133.84 (C arom). Found, %: C 50.87; H 5.05; Cl 29.87. C<sub>10</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>2</sub>. Calculated, %: C 51.09; H 5.14; Cl 30.16.

**2-Iodo-1-methoxy-1-phenylethane (XI).** To a solution of 267 mg (1.05 mmol) of iodine in 8 ml of MeOH was added 275 mg (1.0 mmol) of iodosobenzene dichloride, and the mixture was stirred for 5 min at room temperature. The mixture was poured into a solution of 208 mg (2.0 mmol) of styrene (**II**) in 2.0 ml of MeOH, and the mixture was stirred at room temperature for 10 min. Then it was poured into 30 ml of 5% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Further workup was as described above. We obtained 420 mg (80%) of oily compound (publ. oily compound [5]). <sup>1</sup>H NMR spectrum [400 MHz, CCl<sub>4</sub>-(CD<sub>3</sub>)<sub>2</sub>CO, 3:1, δ, ppm, *J*, Hz]: 3.21 s (3H, OCH<sub>3</sub>), 3.23 m (2H, CH<sub>2</sub>), 4.21 d.d (1H, *J* 5.0, 8.0), 7.26–7.34 m (5H arom). <sup>13</sup>C NMR spectrum [CCl<sub>4</sub>-(CD<sub>3</sub>)<sub>2</sub>CO, 3:1, δ, ppm]: 10.10 (CH<sub>2</sub>I), 56.94 (OCH<sub>3</sub>), 83.55 (CH), 126.51, 128.23, 128.53, 139.98 (C arom). Found: *m/z* 261.98537 [*M*]<sup>+</sup>. C<sub>9</sub>H<sub>11</sub>IO. Calculated: *M* 261.98564. Mass spectrum (Electron impact, 70 eV), *m/z* (*I*<sub>rel</sub>, %): 262 (>1), 135 (14), 121 (100), 104 (10), 103 (9), 91 (10), 77 (13).

NMR spectra were registered on spectrometer Bruker AM-400 (400.13 MHz for <sup>1</sup>H, 100.61 MHz for <sup>13</sup>C spectra) for compound **XI**, the NMR spectra of all other compounds were registered on spectrometer Bruker DRX-500 (500.13 MHz for <sup>1</sup>H, 125.76 MHz for <sup>13</sup>C spectra). NMR and mass spectra were measured and elemental analyses were carried out at TsKP, Siberian Division, Russian Academy of Sciences (grant of the Russian Foundation for Basic Research no. 00-03-40135).

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