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SHORT COMMUNICATIONS

Iodination and Iodonitration of Phenylacetylene under Solvent-Free Conditions

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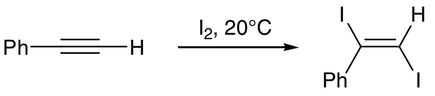
In the recent time, development of the "green chemistry" principles has stimulated studies on organic processes occurring in the absence of a solvent [1]. We have found that phenylacetylene (**I**) reacts with molecular iodine on grinding in a mortar without a solvent for 2–10 min to give 45–90% of *trans*-1,2-diiodo-1-phenylethene (**II**).



I **II**

The yield of diiodide **II** depends on the reactant ratio; the maximal yield was attained when 2 equiv of alkyne **I** was added in portions to 1 equiv of iodine. The absence of by-products in the reaction mixture allowed us to presume that the yield of diiodo derivative **II** may be quantitative when the reaction is performed in a closed system (ball mill) with equimolar amounts of the reactants. Thus, unlike known methods for the synthesis of diiodostyrene which require the use of toxic reagents and complex conditions [2–7], the solvent-free procedure is extremely simple and easy to perform.

Addition of sodium nitrate to the reaction mixture did not change the reaction direction, and no iodonitration product was formed (as in the reaction carried out in acetic acid [8, 9]). Phenylacetylene turned out to be inactive toward another iodonitrating system, KI–$NaNO_3$. Presumably, redox transformation of KI to produce I_2 (which is necessary for generation of the reactive species, nitryl iodide) does not occur in the absence of glacial acetic acid. In order to promote formation of INO_2, concentrated nitric acid was added to the reaction mixture to enable required redox reactions.

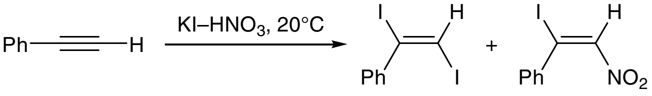
$$4HNO_3 + 2KI \longrightarrow 2NO_2 + I_2 + 2KNO_3 + 2H_2O$$

$$2NO_2 \rightleftharpoons N_2O_4$$

$$I_2 + N_2O_4 \rightleftharpoons 2INO_2$$

By grinding alkyne **I** with KI and HNO_3 in a mortar we obtained a mixture of diiodostyrene **II** and iodonitrostyrene **III**. This result indicates, on the one hand, that the presence of an oxidant is necessary to generate the iodonitrating agent and, on the other, that INO_2 can be formed in the absence of an organic solvent. One more important advantage of the proposed conditions is that they prevent side processes which accompany the reaction performed in acetic acid [8, 9].

In order to elucidate the role of nitrate and the nature of metal cation therein we examined the reactions of phenylacetylene with KI–HNO_3 in the presence of $NaNO_3$ and $Mg(NO_3)_2 \cdot 6H_2O$. We found that addition of $NaNO_3$ does not favor formation of iodo-



I **II** **III**

Reactant ratio	Yield of **II**, %	Yield of **III**, %
I–KI–HNO_3 1.0 : 2.0 : 4.0	50	28
I–KI–HNO_3–$NaNO_3$ 1.0 : 2.0 : 4.0 : 2.0	39	31
I–KI–HNO_3–$Mg(NO_3)_2$ 1.0 : 2.0 : 4.0 : 2.0	34	65

nitration product **III**. By contrast, the yield of compound **III** increased more than twofold in the presence of $Mg(NO_3)_2 \cdot 6H_2O$; correspondingly, the yield of diiodide **II** fell down. The reason is that magnesium nitrate is known [10] to possess a unique ability to bind N_2O_4 as $Mg(NO_3)_2 \cdot N_2O_4$ adduct, thus holding it in the reaction mixture.

Our results clearly demonstrate advantages of the proposed procedure for the iodonitration of phenylacetylene, as compared to that described previously [8, 9]: the reaction is much more selective (two products are formed instead of five as in [8, 9]), the reaction time shortens from 4 h to 5 min, and the temperature is reduced from 85°C to ambient.

Reaction of phenylacetylene (I) with iodine. Phenylacetylene (**I**), 2.0 mmol, was added in portions over a period of 10 min to 1.0 mmol of iodine under grinding in an agate mortar at 20°C. The mixture was extracted with 10 ml of diethyl ether, the extract was washed with 5.0 ml of a 5% solution of $Na_2S_2O_3$, 10 ml of water, and 50 ml of a saturated solution of NaCl, and dried over Na_2SO_4, and the solvent was distilled off to obtain 320 mg (90%) of 1,2-diiodo-1-phenylethene (**II**) with mp 75–76°C; published data [4]: mp 76°C. ^{1}H NMR spectrum, δ, ppm: 7.19 s (1H, =CH), 7.36 s (5H, H_{arom}).

Reaction of phenylacetylene (I) with KI–HNO_3–$Mg(NO_3)_2 \cdot 6H_2O$. A mixture of 2.0 mmol of KI, 2.0 mmol of $Mg(NO_3)_2 \cdot 6H_2O$, and 1.0 mmol of phenylacetylene (**I**) was ground in an agate mortar, 4.0 mmol of 63% HNO_3 was added under continuous grinding, and the mixture was ground for 5 min and extracted with 10 ml of diethyl ether. The extract was washed with 5.0 ml of a 5% solution of $Na_2S_2O_3$, 2× 10 ml of water, and 10 ml of a saturated solution of NaCl and dried over Na_2SO_4, the solvent was distilled off, the residue was dissolved in hexane–benzene (1 : 1), and the solution was applied to a column charged with silica gel. The column was eluted with hexane to isolate 121 mg (34%) of compound **II**, mp 76–77°C [4] and 179 mg (65%) of 1-iodo-2-nitro-1-phenylethene (**III**) as a mixture of *E* and *Z* isomers. The *E* isomer of **III** was partially isolated from the isomer mixture by recrystallization from hexane, mp 49–50°C; published data [11]: mp 49–50°C.

(*E*)-1-Iodo-2-nitro-1-phenylethene (IIIa). ^{1}H NMR spectrum, δ, ppm: 7.36 m (5H, H_{arom}), 7.74 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 113.9 (CI); 127.3, 128.5, 130.3, 138.5 (C_{arom}); 142.9 (CNO_2).

(Z)-1-Iodo-2-nitro-1-phenylethene (IIIb). ^{1}H NMR spectrum, δ, ppm: 77.50 m (5H, H_{arom}), 7.67 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 110.3 (CI); 128.8, 129.0, 131.2, 139.3 (C_{arom}); 143.1 (CNO_2).

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV-300 instrument at 300 and 75 MHz, respectively, using $CDCl_3$ as solvent and TMS as internal reference. The melting points were determined on a Boetius melting point apparatus. Silica gel L (40–100 μm, Chemapol) was used for column chromatography; TLC analysis was performed on Sorbfil plates (PTSKh-AF-A-UF and PTSKh-P-A-UF).

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