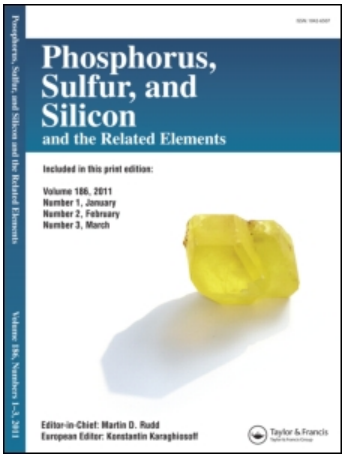

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REACTION OF METALLATED ACETYLENES WITH PHENYLSULFINYLAMINE

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Lithiated alkynes or alkynylmagnesium bromides readily (THF, −30 + 30°C, 10–15 min) react with phenylsulfinylamine to form *N*-phenylalkynyl-1-sulfinamides in high yield. Sequential treatment of but-2-yne with butyllithium and magnesium bromide in THF at −100°C leads to the formation of not only *N*-phenylbut-2-yne-1-sulfinamide, but its allenic isomer, *N*-phenylbuta-2,3-diene-2-sulfinamide in total yield 95%, molar ratio = 2.5:1, respectively. The reaction of prop-1-yne-3-magnesium bromide with phenylsulfinylamine proceeds in diethyl ether at −100°C to afford *N*-phenylprop-2-yne-1-sulfinamide in 81% yield. In no case the probable cyclization is observed.

Keywords: phenylsulfinylamine; alkynes; allenes; butyllithium; metallation; sulfinamides

INTRODUCTION

It has been reported[1] that organylethynylmagnesium bromides react with arenesulphinylamines at a low temperature (-60°C) to give *N*-aryl(organylethynyl)sulfinamides in 20–32% yield. Later[2] a reaction of lithiated 3,3-dimethylbut-1-yne with phenylsulfinylamine (-10 – 0°C) leading to 3,3-dimethyl-*N*-phenylbut-1-yne-1-sulfinamide in 92% yield was carried out by one of us.

To gain a better insight into the reaction of metallated acetylenes with organylsulfinylamines, in particular, to elucidate a possibility of involvement of disubstituted alkynes, to extend the preparative potential of the

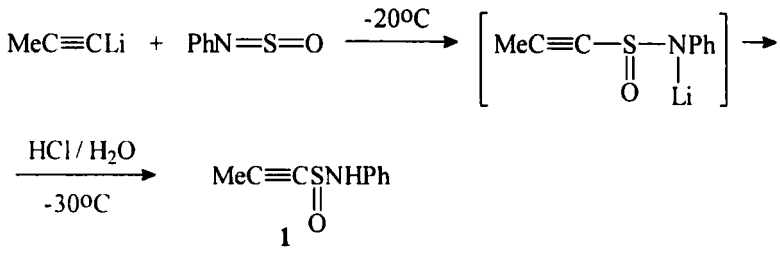
* Correspondence.

reaction and to synthesize new representatives of acetylenic sulfinamides, we have investigated the reaction of metallated alkynes and 3-bromoprop-1-yne with readily accessible phenylsulfinylamine.[3]

RESULTS AND DISCUSSION

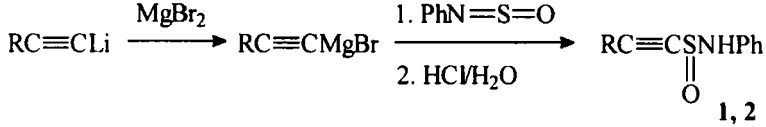
With prop-1-yne and pent-1-yne as examples it was shown that lithiated alkynes react with phenylsulfinylamine to form the corresponding sulfinamides in high yield.

Thus, a sequential treatment of prop-1-yne in organic solvent (THF, hexane, ether) by butyllithium, phenylsulfinylamine and aqueous HCl (temperature range from −30 to 30°C, reaction time 10–15 min) leads to *N*-phenylprop-1-yne-1-sulfinamide **1** in 82% yield (Scheme 1).



SCHEME 1

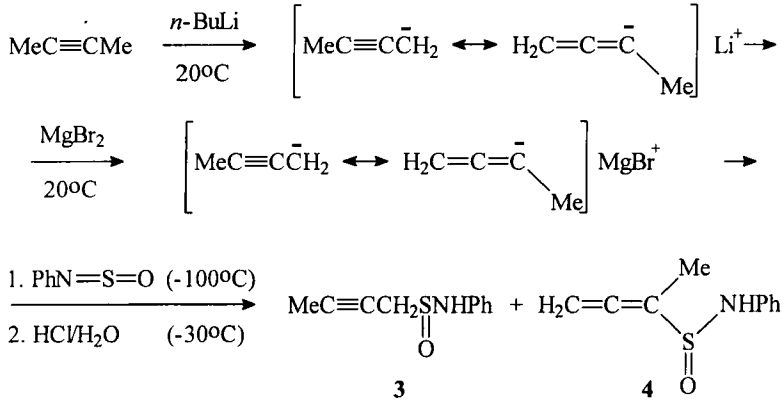
The reaction efficiency is slightly enhanced by a supplementary magnesium bromide treatment of the intermediate lithium derivative (Scheme 2). In this case the yield of sulfinamide **1** reaches 91%. The same conditions were used for an advantageous synthesis of *N*-phenylpent-1-yne-1-sulfinamide **2** (yield 95%) from pent-1-yne and phenylsulfinylamine (Scheme 2).



R = Me (**1**), *n*-Pr (**2**)

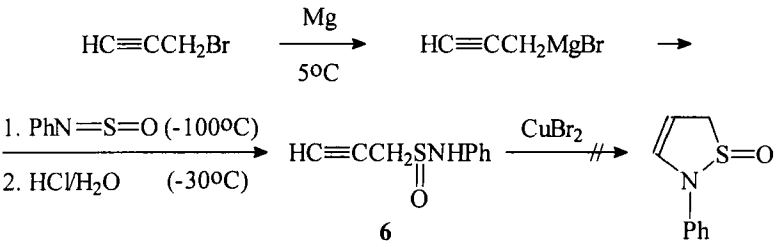
SCHEME 2

It was found that disubstituted alkynes could also be involved in the reaction with phenylsulfinylamine. Thus, under the reaction conditions presented in Scheme 1, 2, but at a lower temperature (-100°C) in a stage of addition of phenylsulfinylamine to the reaction mixture, but-2-yne reacts with phenylsulfinylamine resulting in the formation of *N*-phenyl-but-2-yne-1-sulfinamide **3** and *N*-phenylbuta-2,3-diene-2-sulfinamide **4** in a molar ratio of 2.5:1 (Scheme 3).



SCHEME 3

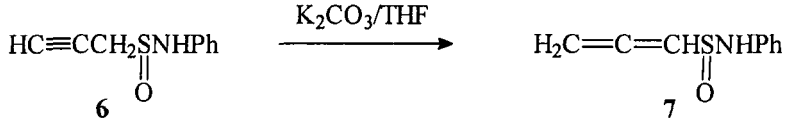
One could expect that under the reaction conditions presented in Scheme 3 prop-1-yne-3-magnesium bromide would react with phenylsulfinylamine analogously through the intermediate akin to **5** to afford two isomers. However, with prop-1-yne-3-magnesium bromide the reaction proceeds selectively resulting in *N*-phenylprop-2-yne-1-sulfinamide **6** in 81% yield (Scheme 4).



SCHEME 4

In this reaction, the fact that only the acetylenic isomer **6** is formed suggests the above acetylene-allene isomerization (Scheme 3) to occur in the stage involving the interaction of but-2-yne with butyllithium.

It should be noted that when heated (50°C, 0.5 h) in the presence of $CuBr_2$, acetylenic compound **6** undergoes no change (no expected cyclization took place) (Scheme 4), whereas in the K_2CO_3/THF system (50°C, 0.5 h) compound **6** shows (^{1}H NMR) a 20% conversion to *N*-phenylallene-1-sulfinamide **7** (Scheme 5).



SCHEME 5

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) NMR spectrometer using TMS as internal standard. IR spectra were obtained with a "Perkin Elmer 283" IR spectrophotometer. All reactions were conducted under anhydrous conditions in an atmosphere of N_2. *n*-BuLi was purchased from Chemetall (Germany) as a 1.6 M solution in hexane. THF was dried over freshly machine-powdered KOH (50 g/L) and distilled over $LiAlH_4$ in the presence of benzophenone under N_2.

N-Phenylprop-1-yne-1-sulfinamide 1

A. Prop-1-yne from a cylinder was introduced into a stirred solution of *n*-BuLi (60 mmol) in 50 ml of THF and 35 ml of hexane cooled to −15 + −10°C until white suspensions were formed. The reaction is exothermic (the temperature rose to 30°C). The temperature was lowered to −20°C and the solution of phenylsulfinylamine (40 mmol) in 20 ml of Et_2O was introduced in one portion. After efficient stirring at −30°C during 10 min, the reaction mixture was hydrolyzed by quickly adding a mixture of 6 g of 36% HCl and 50 ml of icewater. After separation of the layers and extraction of the aqueous layer with ether, the combined organic fraction was

washed with water, dried over $MgSO_4$ and the solvents removed on a rotary evaporator to give a yellow viscous liquid to which 10 ml of Et_2O was added. The solution was placed into a refrigerator for 1.5–2 h. After filtration, washing with pentane and drying *in vacuo* 5.9 g (82%) of cream-colour crystals of **1** (m.p. 93°C) were obtained. ^1H NMR ($CDCl_3$, δ, ppm): 1.83 s (3H, CH_3), 7.15 m (5H, Ph), 7.8 s (1H, NH).

B. Prop-1-yne from a cylinder was introduced into a stirred solution of *n*-BuLi (60 mmol) in 50 ml of THF and 35 ml of hexane cooled to −15 ÷ −10°C until white suspensions were formed. When the temperature of the reaction mixture was allowed to rise to 20°C, the solution of $MgBr_2$ (60 mmol) in Et_2O was added. The temperature was lowered to −10°C and the solution of phenylsulfinylamine (40 mmol) in 20 ml of Et_2O was introduced in one portion. After efficient stirring at −30°C during 10 min, the above work-up was carried out to give 6.8 g (91%) of cream-colour crystals of **1** (m.p. 93°C). ^1H NMR ($CDCl_3$, δ, ppm): 1.95 s (3H, CH_3), 7.28 – 7.20 m (6H, PhNH).

N-Phenylpent-1-yne-1-sulfinamide 2

Pent-1-yne (60 mmol) was introduced into a stirred solution of *n*-BuLi (60 mmol) in 50 ml of THF and 35 ml of hexane cooled to – 25 ÷ −30°C. When the temperature of the reaction mixture was allowed to rise to −15°C, the solution of $MgBr_2$ (60 mmol) in Et_2O was added. The temperature was lowered to - 25°C and the solution of phenylsulfinylamine (40 mmol) in 20 ml of Et_2O was introduced in one portion. After efficient stirring at −30°C during 10 min, the above work-up was carried out to give 8 g (95%) of **2** (light yellow liquid). ^1H NMR ($CDCl_3$, δ, ppm): 0.93 t (3H, CH_3), 1.51 m (2H, CH_2), 2.27 m (2H, $CH_2C\equiv$), 7.21 m (5H, Ph), 7.54 s (1H, NH).

Reaction of but-2-yne with phenylsulfinylamine

But-2-yne (70 mmol) was introduced into a stirred solution of *n*-BuLi (60 mmol) in 50 ml of THF and 35 ml of hexane cooled to −15°C. After addition, the cooling bath with liquid nitrogen was removed and the mixture was stirred at room temperature for 0.5 h. Then the solution of $MgBr_2$ (60 mmol) in Et_2O was added. The temperature was lowered to −100°C and the solution of phenylsulfinylamine (40 mmol) in 20 ml of Et_2O was

introduced in one portion. After the above work-up 7.21 g (95%) of the mixture of **3** and **4** (2.5:1 respectively according to NMR-analysis) were obtained. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.85 t (CH_3 in **3**), 1.95 t (CH_3 in **4**), 3.72 m (CH_2SO in **3**), 5.25 m ($H_2C=$ in **4**), 7.12 m (PhNH). IR (film, cm^{-1}): $\nu_{S=O}$ 1070, ν_{Ph}1610, $\nu_{C=C=C}$ 1965, $\nu_{C\equiv C}$ 2240, ν_{NH} 3210.

N-phenylprop-2-yne-1-sulfinamide 6

Prop-1-yne-3-magnesium bromide prepared beforehand from bromoprop-1-yne (70 mmol) and Mg at 5°C in dry Et_2O was added to a solution of phenylsulfinylamine (40 mmol) in 100 ml of Et_2O cooled to −100°C. The temperature of the reaction mixture was allowed to rise to −30°C. After the above work-up, cooling in a refrigerator for 2 h, filtration, washing with Et_2O and drying *in vacuo* 5.8 g (81%) of white crystals of **6** (m.p. 77°C) were obtained. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.45 s (1H, HC≡), 3.76 m (2H, CH_2SO), 7.28 – 7.10 m (6H, PhNH). Calcd for C_9H_9NOS (179.24): C, 60.34; H, 5.03; N, 7.82; S, 17.88. Found: C, 60.64; H, 5.33; N, 7.94; S, 17.72%.

Isomerization of 6

To a solution of sulfinamide 6 (1 mmol) in 10 ml of THF 0.01 g of K_2CO_3 was added. After heating at 50°C for 0.5 h the reaction mixture was filtered and the solvent removed. The mixture of **6** and **7** was obtained according to NMR-analysis. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.46 s (HC≡ in **6**), 3.76 m (2H, CH_2SO in **6**), 5.30 m ($H_2C=$ in **7**), 6.24 m (HC= in **7**), 7.10 m (PhNH).

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