Pergamon

Tetrahedron Letters, Vol. 37, No. 23, pp. 4051-4054, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00730-7

A Novel Method of C-C Bond Formation *via* Phenylation of Terminal Acetylenes by Triphenylbismuth Difluoride

Sergei A. Lermontov*, Igor M. Rakov and Nikolai S. Zefirov*
Institute of Physiologically Active Substances, Rus. Acad. Sci.,
Chernogolovka, Moscow Region, 142432, Russia.

Peter. J. Stang
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

Abstract: Terminal acetylenes readily undergo phenylation by Ph_3BiF_2 in the presence of catalytic amounts of CuCl affording phenyl substituted acetylenes.

Organobismuth (V) compounds are known to be useful arylating reagents for a large variety of substrates. They accomplish O- and N- arylation of alcohols and amines[1,2] respectively and, even more interesting, C- arylation of phenols, enols and some carbaniones, thus affording a novel method of C-C bond formation[3,4]. However, we were unable to find examples of the arylation reactions of acetylenes by organobismuth compounds in the literature.

Therefore, we describe here the reaction of direct phenylation of terminal acetylenes by triphenylbismuth difluoride Ph_3BiF_2, 1, in the presence of catalytic amounts of cuprous chloride CuCl. The reaction proceeds at reflux in benzene or toluene solutions, the best acetylene to 1 ratio being 2 : 1.

Thus, phenylacetylene, 2, affords diphenylacetylene (tolan), 3, in high yield almost without contamination (eq. 1, all yields are based on Ph_3BiF_2 and 2 : 1 stoichiometry)

$$\underset{2}{PhC{\equiv}CH} + \underset{1}{Ph_3BiF_2} \xrightarrow[\text{reflux 1 h}]{CuCl,\ C_6H_6} \underset{3\ (87\%)}{PhC{\equiv}CPh} + \underset{4\ (0.7\%)}{Ph\text{-}Ph} \qquad (1)$$

Other organobismuth compounds - Ph_3BiCO_3 and Ph_3BiCl_2 gave much smaller yields (20% and traces respectively). The yields also decreased significantly (26% of 3) if 1 and 2 were taken in 1 : 1 ratio. Only traces of products could be detected in the absence of CuCl.

Reflux in toluene afforded 3 and 4 in 70% and 9% yields respectively.

Similar results were obtained with silylated phenylacetylene 5 in benzene and toluene (1 : 5 = 1 : 2) (eq. 2).

$$\underset{\mathbf{5}}{\mathrm{PhC{\equiv}CSi(CH_3)_3}} \xrightarrow[\text{reflux, 1-2 h}]{\text{1, CuCl}} \underset{\mathbf{3}\ (59\%)}{\mathrm{PhC{\equiv}CPh}} + \underset{\mathbf{4}\ (3\%)}{\mathrm{Ph\text{-}Ph}} + \underset{\mathbf{6}\ \text{(traces)}}{\mathrm{[PhC{\equiv}C]_2}} \qquad (2)$$

On the whole the reaction between **1** and silylacetylene **7** in 1 : 2 ratio proceeds in the same manner in both benzene and toluene (eq. 3).

$$\underset{\mathbf{7}}{\mathrm{HC{\equiv}CSi(CH_3)_3}} \xrightarrow[\text{reflux, 1-3 h}]{\text{1, CuCl}} \underset{\mathbf{2}\ (16\%)}{\mathrm{PhC{\equiv}CH}} + \underset{\mathbf{4}\ (1\%)}{\mathrm{Ph\text{-}Ph}} + \underset{\mathbf{5}\ (20\%)}{\mathrm{PhC{\equiv}CSi(CH_3)_3}} \qquad (3)$$

$$+ \underset{\mathbf{3}\ (60\%)}{\mathrm{PhC{\equiv}CPh}}$$

In this case diacetylene HC≡C-C≡CH might have been lost (if it appeared at all) because of its volatility. It is interesting to note that the trimethylsilyl group is substituted by the phenyl group with the same facility as the proton.

The phenylation reaction could be extended on acetylenes bearing alkyl substituents at the triple bond. Thus, 1-hexyne, **8**, and its silyl derivative **9** readily form phenylated product - butylphenyl acetylene, **10**, under the action of **1** and CuCl (eq. 4)

$$\mathrm{n\text{-}BuC{\equiv}CR} \xrightarrow[\text{reflux}]{\text{1, CuCl}} \mathrm{n\text{-}BuC{\equiv}CPh} + \mathrm{Ph\text{-}Ph} \qquad (4)$$

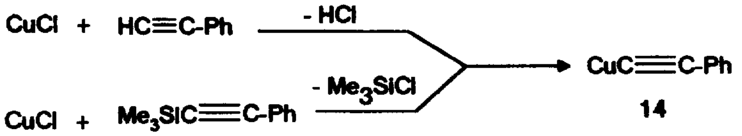
	10	4
8 R = H, benzene, 1 h	15%	13%
toluene, 1.5 h	35%	36%
9 R = SiMe$_3$, benzene, 1 h	48%	33%
toluene, 1 h	40%	16%

Analogously, benzylpropargyl ether, **11**, and its silyl derivative **12** are phenylated as well by **1** in either benzene or toluene (eq. 5)

$$\mathrm{PhCH_2OCH_2C{\equiv}CR} \xrightarrow[\text{reflux}]{\text{1, CuCl}} \mathrm{PhCH_2OCH_2C{\equiv}CPh} + \mathrm{Ph\text{-}Ph} \qquad (5)$$

	13	4
11 R = H, toluene, 2 h	55%	2.5%
benzene, 4 h	48%	16%
12 R = SiMe$_3$, toluene, 2 h	39%	14%
benzene, 1 h	24%	-

We think that the mechanism of the phenylation reaction includes the formation of an intermediate pentaorganyl bismuth compound $\mathrm{Ph_3BiR_2}$ (where R is an acetylenic residue). The necessary 1 : 2 ratio of **1** to acetylene confirms this suggestion. Such pentavalent bismuth compounds are not extensively investigated - we could only find data concerning the formation and termal decomposition of pentaphenyl bismuth to form biphenyl Ph-Ph and triphenylbismuth Ph_3Bi [5a], reactions with a number of electrophilic reagents[5a] and some examples of phenylation reaction[3,5b]. Cuprous chloride CuCl probably plays the role of metallating agent providing cuprous acetylenide 14 according to eq. 6, (an easy formation of cuprous acetylenides in the reaction between cuprous salts and acetylenes is documented in the literature[6]).



(6)

14

The acetylenide reacts with the difluoride 1 to give the pentacovalent bismuth compound Ph_3BiR_2 (and regenerates the catalyst - Cu^+ cation) which further decomposes termally like Ph_5Bi affording the products of reductive coupling at the bismuth atom (eq. 7).

$$1 + \underset{14}{2CuC{\equiv}CPh} \xrightarrow{-CuF} \left[Ph_3Bi(C{\equiv}CPh)_2\right] \longrightarrow PhC{\equiv}CPh + \left[Ph_2BiC{\equiv}CPh\right] \quad (7)$$

To confirm this suggestion we carried out the reaction of preformed 14 with 1 in 2 : 1 ratio in benzene and found that indeed tolan, 3, formed together with Ph-Ph, 4 (eq. 8)

$$\underset{1}{Ph_3BiF_2} + \underset{14}{2CuC{\equiv}CPh} \xrightarrow[\text{reflux, 1 h}]{\text{benzene}} \underset{3\ (17\%)}{PhC{\equiv}CPh} + \underset{4\ (40\%)}{Ph\text{-}Ph} \quad (8)$$

We did not study the bismuth containing products (probably $Ph_2BiC{\equiv}CR$ or its mixture with Ph_3Bi, $(RC{\equiv}C)_2BiPh$, etc.).

To determine the origin of Ph-Ph, 4, we heated 1 in benzene during 1 h and found that it produced 4 in 40% yield. This fact seems to confirm that in all cases Ph-Ph is formed mainly from 1 and not from the pentaorganyl bismuth compound $Ph_3Bi(C{\equiv}CR)_2$.

Thus, we may conclude, that triphenylbismuth difluoride, 1, appears to be a novel reagent for a direct phenylation of terminal acetylenes and hence, a novel source for C-C bond formation.

A typical procedure: 0.53 g ($1.109 * 10^{-3}$ mol) of 1[7], 0.226 g ($2.22 * 10^{-3}$ mol) of 2 and 0.022 g ($2.2 * 10^{-4}$ mol) of CuCl in 6 mL of dry benzene were refluxed during 1 h in Ar atmosphere. The reaction mixture was analysed by GL chromatography using internal standard and 87% of diphenylacetylene 3, 0.7% of biphenyl 4 and 5% of starting 2 (based on 1 : 2 stoichiometry) were observed. Column chromatography (SiO_2 - hexane) afforded 3 in 68% (0.168 g) isolated yield. Mp 59 - 60 °C, MS (70 eV) 178, the retention time of the sample coincides with that of commercially available tolan on two chromatographic columns of different polarity (SE-30, XE-60) [10].

REFERENCES AND NOTES.

1. Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *Zh. Obshch. Khim.* (Russ.) **1984**, *54*, 2157 - 2158; Barton, D. H. R.; Finet, J-P.; Khamsi, J.; Pichon, C. *Tetrahedron Lett.* **1986**, *27*, 3619 - 3622; Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *Zh. Obshch. Khim.* (Russ.) **1985**, *55*, 2514 - 2519.
2. Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *Zh. Obshch. Khim.* (Russ.) **1985**, *55*, 466 - 467; Barton, D. H. R.; Finet, J- P.; Pichon, C. *J. Chem. Soc., Chem. Commun.* **1986**, 65 - 66.
3. Barton, D. H. R.; Bhatnagar, N. Y.; Blazejewski, J- C.; Charpiot, B.; Finet, J- P.; Lester, D. J.; Motherwell, W. B.; Barros Papoula, M. T. .; Stanforth, S. P. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2657 - 2665.
4. Barton, D. H. R.; Blazejewski, J- C.; Charpiot, B.; Finet, J- P.; Motherwell, W. B.; Barros Papoula, M. T.; Stanforth, S. P. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2667 - 2675; Barton, D. H. R.; Finet, J- P.; Giannotti, C.; Halley, F. *J. Chem. Soc., Perkin Trans. 1*, **1987**, 241 - 249.
5. a. Wittig, G.; Clauβ, K. *Annalen*, **1952**, *578*, 136 - 146; Razuvaev, G. A.; Osanova, N. A.; Sharutin, V. V. *Dokl. Akad. Nauk SSSR*, (Russ.) **1975**, *225*, 581 - 582; Razuvaev, G. A.; Osanova, N. A.; Sharutin, V. V. Sorokin, A. I.; Okhlopkova, I. E. *Dokl. Akad. Nauk SSSR*, (Russ.) **1978**, *238*, 361 - 363; b. Barton, D. H. R.; Blazejewski, J- C.; Charpiot, B.; Lester, D. J.; Motherwell, W. B.; Barros Papoula, M. T. *J. Chem. Soc., Chem. Commun.* **1980**, 827 - 829.
6. Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313 - 3315.
7. The starting **1** was prepared either from Ph_3Bi and XeF_2 or from Ph_3BiCl_2 and KF according to a literature procedure[8] and had the mp 160 °C and ^{19}F NMR (CF_3COOH): -83 ppm. Lit : ^{19}F NMR: -81 ppm[9]. Mp 158.5 - 159 °C[8].
8. Challenger, F.; Wilkinson. J. F. *J. Chem. Soc.*, **1922**, *121*, part I, 91 - 104.
9. Muetterties, E. L.; Mahler, W.; Packer, K. J.; Schmutzler, R. *Inorg. Chem.*, **1964**, *3*, 1298 - 1303.
10. Phenylation of **5**, **7**, **8**, **9**, **11** and **12** is performed analogously, the products and their concentrations were determined by GLC. 1,4-diphenyldiacetylene **6**[11] and acetylene **10**[12] for the comparison were synthesised independently by the known procedures. **13** was prepared from benzyl chloride and lithium derivative of 3-phenylprop-2-yne-1-ol
11. Eglinton, G.; Galbraith, A. R. *J. Chem. Soc.*, **1959**, part I, 889 - 896.
12. Schlubach, H. H.; Repennig, K. *Annalen*, **1958**, *614*, 37 - 46.

Acknowledgement. This work was supported by the Russian Foundation of Fundamental Investigations (Grant No. 94-03-08654) and by the FIRCA of NIH (R03TW00437).

(*Received in UK* 10 *November* 1995; *revised* 18 *April* 1996; *accepted* 19 *April* 1996)