Pergamon

Tetrahedron Letters, Vol. 35, No. 27, pp. 4777-4780, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00901-5

DBU/DMSO Promoted Dehydrobromination of 1,1-Dibromoolefins. A General Synthesis of 1-Bromoaromatic Alkynes under mild Conditions

Victorin Ratovelomanana*, Yolande Rollin, Catherine Gébéhenne,
Corinne Gosmini and Jacques Périchon

Unité Mixte de Recherche C.N.R.S., d'Electrochimie, Catalyse et Synthèse Organique,
2, rue Henri-Dunant 94320 Thiais (France)

Abstract *- A new procedure for the synthesis of 1-Bromoalkynes by DMSO/DBU induced dehydrobromination of 1,1-dibromoethylenes under mild conditions is described.*

The aim of the present work is to describe a new procedure for the synthesis of 1-bromoaromatic alkynes, which are important intermediates in organic chemistry. Unsymmetrical poly(phenylacetylene) derivatives which constitute a novel class of organic materials are being actively studied[1]. The most common route for the synthesis of unsymmetrical diynes or conjuguated polyynes is the Cadiot-Chodkiewicz reaction[2], involving a copper-catalyzed condensation of terminal acetylenes with 1-haloalkynes. The general synthesis of 1-haloalkynes has been reviewed[3,4].

An efficient process in which an aldehyde can be transformed by chain extension to a 1,1-dibromoolefin would be of considerable value[5] (Scheme 1).

$$\text{Ar-CHO} \rightarrow \text{ArCH=CBr}_2 \xrightarrow{?} \text{Ar-C}\equiv\text{C-Br}$$

Scheme 1

To our best knowledge, few procedures report the transformation of 1,1-dibromoalkenes into the corresponding 1-bromoalkynes[6]. Pale and coworkers[7] reported that the treatment of 1,1-dibromovinylepoxide with sodium bis(trimethylsilyl)amide at low temperature (- 105°C) provides the corresponding 1-bromoepoxyacetylene in high yield. However, they made no comment on the role of base selected. It is well-known that Phase-Transfer-Catalysis (PTC) promoted dehydrohalogenation[8] in organic-aqueous two-phase media. In this way, 1-bromoalkynes were isolated in fair to good yields[9].

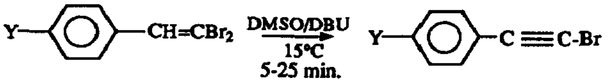
Searching for the agents which may be useful for seach transformation, we have studied the influence of various reaction parameters : nature of base, nature of solvent, relative proportion of reactants and temperature. In a preliminary experiment, in order to determine the relative efficiencies of various bases, we found that triethylamine does not work : the starting materials are entirely recovered. The use of 1,1, 3,3-tetramethylguanidine (TMG)[10] or 1,5-diazabicyclo[4.3.0] non-5-ene (DBN)[11a] gives the desired product with concomitant formation of unidentified by-products. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), a non nucleophilic and extremely strong base become useful reagent in organic chemistry[11]. Oediger and Moller reported that DBU dehydrobrominates 2-bromoalkanes in good yields, with a regioselectivity in favour of the Saytzef products[12]. We found that DBU promotes the dehydrobromination of 1,1-dibromoalkenes remarkably well. However the best results are obtained when the transformations are carried out in DMSO at room temperature.

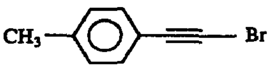
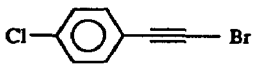
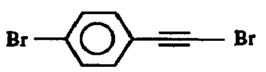
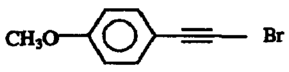
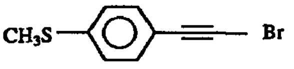
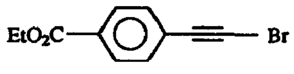
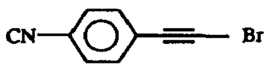
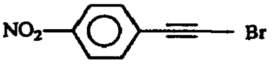
The efficiency of solvents decreases in the order

$$DMSO > DMF > CH_3CN \gg THF$$

Our results are depicted on the table.

Table : DMSO/DBU promoted dehydrohalogenation on 1,1-dibromoaromatic olefins.



Entry	Y	Product^{a}	Yield^{b} (%)	Mp
1	CH_3		80	c
2	Cl		95	88-90
3	Br		92	96-97
4	CH_3O		86	39-41
5	CH_3S		90	57-60
6	CO_2Et		90	111-113
7	CN		95	150-151 (dec)
8	NO_2		92	180-182 (dec)

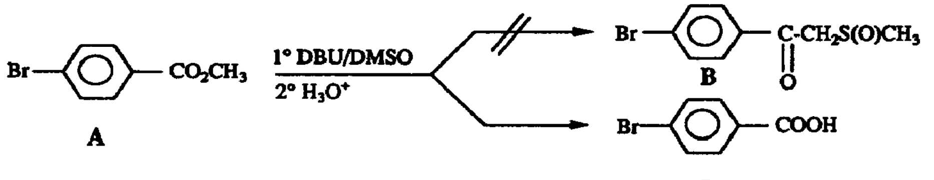
a) All compounds were characterized by ^{1}H, ^{13}C NMR, FT-IR and GC/MS analysis.
b) isolated yields. c) Bp$_{14}$97-98°.

It has been reported that when *sec*- and *tert*-benzylic alcohols or *tert*-aliphatic alcohols are heated in DMSO, dehydratation produced olefins in good yields[13]. DMSO, a polar aprotic solvent with excellent solvating power for organic compounds, acts as a nucleophile at either the oxygen or sulfur atom[14]. In our case, in the absence of base, no reaction occurs. Optimum results depend - first : on concentration of dibromides, - second on the speed of the addition of DBU. A rapid addition of base leads to a dark solution due to the formation of unidentified polymeric product. At the temperature below 20° C, a slow addition results in slightly coloured solution. In this manner good to excellent yields of desired compounds are obtained. Table illustrates the generality of the reactions and also demonstrates the compatibility of various functionnal groups.

Typical Procedure

At 15°C under argon atmosphere, a solution of vinylic dibromide (10 mM) in DMSO is stirred gently with a magnetic stirring bar. A molar solution of DBU in DMSO (20 mL) is added dropwise (the temperature did not rise by more than 20°C). The progress of the reaction is monitored by GPC. The mixture is neutralized with a cooled solution of 0.5 N HCl. Usual work-up using dichloromethane as solvent followed by filtration on a short column of silica gel (eluant : pentane/ether : 1/1) gave the pure product.

The strong base ability of DBU/DMSO has been reported by Hanessian and Staub[15] in the elimination of mesyl group of carbohydrate derivatives. Sato *et al*[16] suggest the intermediary of "dimsyl" anion in DMSO. The latter is a well-known reaction sequence for the transformation of esters into β-ketosulfoxide[17]. In our conditions, this scenario is not realistic (Table : entry 6). Nevertheless, the treatment of A with DBU/DMSO at 80° C during several hours gives C as a sole product (Scheme 2)



Scheme 2

From these results, the transformation probably could took place in two discrete steps : the first of which is the deprotonation of vinylic dibromide, followed by bromine displacement.

In summary, the present method is advantageous, in comparison with reported procedures from this point of view of the mildness of the reaction conditions, high yields and operational simplicity.

We are very grateful to Mrs Jeanne Périchon for her help in performing the FT-IR experiments.

REFERENCES AND NOTES

1) a) Barraud, J.Y.; Gervat, S.; Fauvarque, J.F.; Ratovelomanana, V. *Eur. Pat., Alcatel NV.* **924020811.** b) Matsuda, H.; Okada, S. ;.Nakanishi, H. ; Kato, M. ; Shigeru, N.; Horiishi, N.; *Jpn Kokai Tokkyo Koho* **JP 62,255,460.** c) Choe, E.W. *Celanese Corp. U.S. Pat.*; **4,703,096.** d) Lee, J. ; Shim, J. *J. Chem. Soc. Chem. Commun.*, **1993** 1420-1422. e) Kwock, E.W.; Bird, T.Jr.; Miller, T.M. *Macromolecules* **1993**, *26*, 2935-2940. f) Polzonetti, G.; Russo, M.V.; Furlani, A.;

Infante, G.; *Chem. Phys. Lett.* **1993**, *214*, 333-337.; . g) Fouquey, C.; Lehn, J.M.; Malthête, J. *J. Chem. Soc. Chem. Commun.*, **1987**, 1424-1426.

2) a) Chodkiewicz, W.; Cadiot, P.; *Compte-Rend. Acad. Sci., (Paris)* **1955**, *241* 1055-1057. b) Chodkiewicz, W.; *Ann. Chim.* **1957**, *2*, 819-869.

3) a) Jager, V. Houben-Weyl *"Methoden der Organishen Chemie"* Ed. Muller vol. V/2a Thieme Verlag Stuttgart **1977**. b) Brandsma, L. *"Preparative Acetylenic Chemistry"* Second Edition Ed. Elsevier Amsterdam 1988.

4) For recent papers see : a) Jeffery, T. *J. Chem. Soc. Chem. Commun.*, **1988** 909-910 b) Braga, L.. A. ; Comasseto, J.V. ; *Synth. Commun.*, **1989**, *19*, 2877-2883. c) Wagner, A.; Heitz, M.P. ; Mioskowski, H. *Tetrahedron Lett* .**1990**, *31*, 3141-3144. d) Casarini, . ; Dembrech, P.; Reginato, G.; Ricci, A., *Tetrahedron Lett.*, **1991**, *32*, 2169-2170. e) Ochiai, M.; Uemura, K..; Masaki, Y. *J. Am. Chem. Soc.*, **1993**, *115*, 2528-2529.

5) a) Ramirez, F.; Desai, N.B.; McKelvie N.; *J. Am. Chem. Soc.*, **1962**, *84*, 1745-1747. b) Corey, E.J.; Fuchs, P.L *Tetrahedron Lett.*, **1972**, 3769-3772.

6) The treatment of 1,1-dichloroalkenes with lithium amides at low temperature (- 60° C) gives 1-chloro-1-alkynes in high yield. See : Villieras, J.; Perriot, P.; Normant, J.F. *Synthesis* **1975**, 458-461.

7) Grandjean, D.; Pale, P.; Chuche, J. *Tetrahedron Lett.*, **1992**, *33*, 5355-5358.

8) Dehmlov, E.; Dehmlov, D. *"Phase Transfer Catalysis"* 3rd, ed ; Verlag Chemie : Weinheim 1993.

9) a) Bestman, H.J.;Frey, H. *Justus Liebigs Ann. Chem.* **1980**, *1180*, 2061-2071. b) Li, P. ; Alper, H. *J. Org. Chem.*, **1986**, *51*, 4354-4356.

10) Dowd, P.; Wilk, B.K.; Wlostowiski, M.; *Synth. Commun.*, **1993**, *23*, 2323-2329 and references therein.

11 a) Oediger, H.; Möller, F.; Either, K. *Synthesis* **1987**, 591-598. b) Hermecz, I.; *Adv. Heterocycl. Chem.*, **1987**, *42*, 84-144. c) Helinski, J.; Dabkowski, W., *Tetrahedron Lett.* **1993**, *34*, 6451-6454. d) Caplar, V.; Skarić, V. *Helv. Chim. Acta* **1993**, *76*, 2553-2562 e) Braverman, S.; Gottlieb, H.E. *Tetrahedron Lett.*, **1994**, *35*, 953-956. f) Erba, C.D.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **1994**, *50*, 3529-3536.

12. Oediger, H.; Möller F. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 76.

13. Traynelis, V.J. ; Hergenrother, W.L.; Livingston, J.R.; Valicenti, J.A.; *J. Am. Chem. Soc.*, **1962**, *84*, 2377-2383.

14. Szmant, H.H. in "Dimethylsulfoxide" eds. W.J. Stanley, E.E. Roebaum and D.C. Wood, Marcel Dekker New-York 1971, vol. 1.

15. Hanessian, S.; Staub, P.A.*Carbohydr. Res.*, **1971**, *16*, 419-433.

16. Sato, K. I.; Kubo, N.; Takada, R.; Sakuma, S. *Bull. Chem. Soc. Jpn.*, **1993**, *66*, 1156-1165.

17. a) Becker, H.D.; Russel, G.A. *J. Org. Chem.* **1963**, *28*, 1896-1898. b) Corey, E.J.; Chaykowski, M. *J. Am. Chem. Soc.*, **1964**, *86*, 1639-1640.

(*Received in France* 8 *April* 1994; *accepted* 5 *May* 1994)