Monatsh Chem 139, 549–551 (2008)
DOI 10.1007/s00706-007-0787-y
Printed in The Netherlands

Monatshefte für Chemie
Chemical Monthly

A facile and convenient method for the conversion of thioamides into amides using pyridinium hydrobromide perbromide

Moslem M. Lakouraj, Keivan Ghodrati

Department of Organic Chemistry, Faculty of Chemistry, Mazandaran University, Babolsar, Iran

Received 7 August 2007; Accepted 16 August 2007; published online 11 April 2008

Abstract Selective transformation of thioamides to their corresponding carbonyl compounds are performed in high to excellent yields under mild conditions using pyridinium hydrobromide perbromide (*PHBP*) as a mild and efficient reagent.

Keywords Pyridinium hydrobromide perbromide; Thioamides; Transformation; Carbonyl compounds.

Introduction

The introduction and removal of functional groups is of great importance in the synthesis of polyfunctional organic molecules. The transformation of thiocarbonyl compounds to their corresponding oxygen analogues has received considerable attention during recent years. Various methods and reagents have been reported for the transformation of thiocarbonyl compounds to their oxo analogues [1–23]. On the other hand, bromine offers a particularly desirable choice for bromination and oxidation of organic compounds because it is inexpensive and commercially available, but it suffers from some serious disadvantages [24]. Owing to the hazards and serious problems associated with bromine, few modified brominating agents, such as bromide perbromide reagents have been reported [24a].

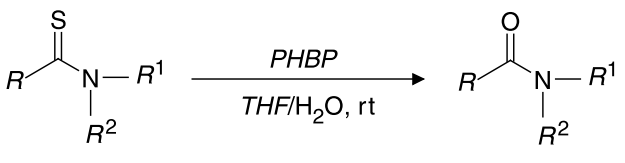
Correspondence: Moslem M. Lakouraj, Department of Organic Chemistry, Faculty of Chemistry, Mazandaran University, Babolsar 47416, Iran. E-mail: lakouraj@umz.ac.ir

Pyridinium hydrobromide perbromide (*PHBP*) has been prepared and used as a selective brominating reagent for ketones, acetals, alkenes, activated phenols, anilines, heterocycles and as oxidation/dehydrogenation reagent [25]. However, literature describing thioamide conversion to amides by using *PHBP* is not available. In connection with our work on hydrobromide perbromide and bromide perbromide reagents, herein we report the chemical transformation of thioamides to their corresponding amides using this reagent.

Results and discussion

This conversion is carried out by stirring the reagent with thioamides in *THF*/H_2O (or dioxane/H_2O) at room temperature under air atmosphere in high yields (Table 1).

As shown in Table 1, a series of thioamides and thioureas (entries 1–21) were reacted with 2 equivalents of the reagent to afford the corresponding car-



1 **2**

Scheme 1

Table 1 Conversion of thioamides into the corresponding amides at room temperature by *PHBP*

Entry	*R*	R^1	R^2	Reaction time/h	Product yield[a]/%	mp or bp/°C [Ref.]
1	*Ph*	H	*Ph*	1.5	88	163 [27a, c]
2	*Ph*	H	CH_2*Ph*	1.5	92	105–106 [27a]
3	*Ph*	H	$CH_2CH_2CH_2CH_3$	1.5	88	42 [27]
4	*Ph*	H	2-$CH_3C_6H_4$	1.5	85	143 [27c]
5	*Ph*	H	4-$CH_3C_6H_4$	1	90	157–158 [27a, c, d]
6	*Ph*	H	4-ClC_6H_4	2	87	192–193 [27d]
7	*Ph*	H	4-*Br*C_6H_4	2	86	202–203 [27a]
8	*Ph*	H	4-$CH_3OC_6H_4$	1.5	83	153 [27c]
9	*Ph*	CH_3	*Ph*	2.5	75	63 [27a, d]
10	*Ph*	*Et*	*Et*	1.5	86	42 [27a, d]
11	4-$NO_2C_6H_4$	H	CH_2*Ph*	3.5	83	142 [27]
12	4-$NO_2C_6H_4$	CH_3	*Ph*	4	76	106–107 [27b]
13	*Ph*	$CH_2CH_2CH_2CH_2CH_2$		2	84	48 [27a]
14	CH_3	H	*Ph*	1.5	85	114 [27a, d]
15	CH_3	H	4-$CH_3C_6H_4$	1.5	89	154 [27a, d]
16	CH_3	H	4-ClC_6H_4	2	83	179 [27a, d]
17	CH_3	H	4-*Br*C_6H_4	2	87	168 [27a]
18	CH_3	CH_3	*Ph*	2.5	79	101–103 [27a]
19	CH_3	H	H	1	73	82 [27a, d]
20	NH_2	H	H	0.5	78	131–132 [27a, d]
21	*Et*NH	H	*Et*	1	79	111 [27e]

[a] Yields refer to isolated yield

Table 2 Comparison of conversion of thiobenzanilide into the corresponding amides by *PHBP* and some common reagents

Entry	Reagent	Condition	Time/h	Yield/%	[Ref.]
1	*Caro*'s acid/SiO_2	CH_3CN/25°C	5	60	[21]
2	$NaNO_2$/HCl (4 *M*)	CH_2Cl_2/20°C	4	65	[14]
3	2-Nitrobenzenesulfonyl chloride/KO_2	CH_3CN/−35°C	6.5	91	[18]
4	*PHBP*	*THF*/H_2O/rt	1.5	88	

bonyl compounds in 73–92% yields within 0.5–4 h. It is noteworthy that the bromination of aromatic rings did not proceed at all during the transformation of thioamides to amides by this reagent. The starting thioamides were easily prepared from the corresponding amides using P_4S_{10} as thiation reagent [26].

Under the same reaction condition, acetals and ketals remained unchanged in the reaction mixture. Therefore, selective transformation of thioamides and thioureas in the presence of acetals or ketals is achievable and can be considered as a noteworthy feature of this method.

In order to show the advantage of the method, we compared the results of transformation of thiobenzanilide into the corresponding amide with some of those reported in literature (Table 2).

In conclusion, we introduced a convenient and selective method for the transformation of thioamides and thioureas using prydinium hydrobromide perbromide (*PHBP*), a versatile, stable, inexpensive, and commercially available reagent.

Experimental

Chemicals were purchased from Fluka. The carbonyl derivatives were prepared from the corresponding carbonyl compounds according to the reported procedure. Products were characterized by comparison of their spectroscopic (IR, ^{1}HNMR, and TLC) and physical data (mp and bp) with those of authentic samples. Infrared spectra were recorded on a Brucker FTIR-85 spectrometer. ^{1}H NMR spectra were recorded with a JEOL FT-NMR 90 MHz (^{1}H) and at 22.4 MHz (^{13}C) in $CDCl_3$ or *DMSO*-d_6 as the solvent and tetramethyl silane (*TMS*) as internal reference. Melting points were measured with Electro thermal 9100 instrument.

General procedure for the transformation of thioamides to amides with PHBP

To a solution of 1 mmol thioamide in 10 cm^3 *THF* and 2 mmol perbromide reagent in a round flask was added 5 cm^3 of H_2O drop-wise within 1 min at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the filtrate was extracted with 2×20 cm^3 CH_2Cl_2. Anhydrous Na_2SO_4 was added to the organic layer, and evaporation of the solvent gave the corresponding carbonyl compounds.

Acknowledgements

Financial support from the research council of Mazandaran University is gratefully acknowledged.

References

1. Mikolajczkyk M, Luczak J (1978) J Org Chem 43:2132
2. Tamagaki S, Hatanaka I, Kozuka S (1977) Bull Chem Soc Jpn 50:3421
3. El-Wassimy MTM, Jorgensen KA, Lawesson S-O (1983) Tetrahedron 39:1729
4. Ley SV, Meerholz CA, Barton DHR (1980) Tetrahedron Lett 21:1785
5. Gano JH, Atik S (1979) Tetrahedron Lett 20:4635
6. Capps HH, Dehn WM (1932) J Am Chem Soc 54:4301
7. Kalm MJ (1961) J Org Chem 26:2925
8. Cussan NJ, Ley SV, Barton DHR (1980) J Chem Soc Perkin Trans 1:1650
9. Mikolajczyk M, Luczak J (1975) Synthesis:114
10. Abuzar S, Sharma S, Lyer RN (1980) Indian J Chem 19B:211
11. Olah GA, Arvanaghi M, Ohannesian L, Surya Prakash GK (1984) Synthesis:785
12. Kochhar KS, Cottrell DA, Pinnick HW (1983) Tetrahedron Lett 24:1323
13. Masuda R, Hojo M, Ichi T, Sasano S, Kobayashi T, Kuroda C (1991) Tetrahedron Lett 32:1195
14. Jorgensen KA, Ghattas A-BAG, Lawesson S-O (1982) Tetrahedron 38:1163
15. Chalais S, Cornelis A, Laszlo P, Mathy A (1985) Tetrahedron Lett 26:2327
16. Ravindranathan T, Chavan SP, Awachat MM, Kelkar SV (1995) Tetrahedron Lett 36:2277
17. Radha Rani B, Rahman MF, Bhalerao UT (1992) Tetrahedron 48:1953
18. Kim YH, Chung BC, Chang HS (1985) Tetrahedron Lett 26:1079
19. Jorgensen KA, El-Wassimy MTM, Lawesson S-O (1983) Tetrahedron 39:469
20. Varma RS, Kumar D (1999) Synth Commun 29:1333
21. Movassagh B, Lakouraj MM, Ghodrati K (2000) Synth Commun 30:2353
22. Mohammadpoor-Baltork I, Sadeghi MM, Esmayilpour K (2003) Phosphorous Sulfur Silicon 178:61
23. Mohammadpoor-Baltork I, Memarian HR, Bahrami K (2004) Monatsh Chem 135:411
24. a) Paquette LA (1995) Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons, New York; b) Fuson RC (1962) Reaction of Organic Compounds, Wiley, New York, p 58; c) Norman ROC, Taylor R (1965) Electrophilic Substitution in Benzenoid Compounds, American Elsevier, New York, p 130
25. a) Fieser LF, Fieser M (1967) Reagents for Organic Synthesis, vol. 1. John Wiley & Sons, New York, p 967; b) Paquette LA (1995) Encyclopedia of Reagents for Organic Synthesis, vol. 6. John Wiley & Sons, New York, p 4370
26. a) Scheeren JW, Ooms PHJ, Nivard RJF (1973) Synthesis: 149; b) Fieser LF, Fieser M (1967) Reagents for Organic Synthesis, vol. 1. John Wiley & Sons, New York, p 333
27. a) Buckingham J, Donaghy SM (1996) Dictionary of Organic Compounds 6th edn. Chapman & Hall; b) Boit H-G, Beilsteins Handbuch der Organischen Chemie, 4. Aufl; c) Vogel's (1989) Textbook of Practical Organic Chemistry, 5th edn. John Wiley & Sons, New York; d) Shriner RL, Fuson RC (1980) The Systematic Identification of Organic Compounds, John Wiley & Sons, New York; e) Asakawa K (2002–2003) TCI Organic Chemicals Catalog; f) Aldrich Ltd (1999–2000) Aldrich Catalogue Handbook of Fine Chemicals