A CONVENIENT SYNTHESIS OF [1,2-a] BENZIMIDAZO-1,3,5-TRIAZIN-4-THIONES AND [1,2-a] BENZIMIDAZO-1,3,5-TRIAZIN-4-ONES

R. ABDERRAHIM, B. HAJJEM, B. BACCAR

Heterocyclic Compounds Laboratory, Department of Chemistry, Faculty of Sciences, University of Tunis, 1060 Tunis, Tunisia.

(Presented in December 1992, accepted in May 1993)

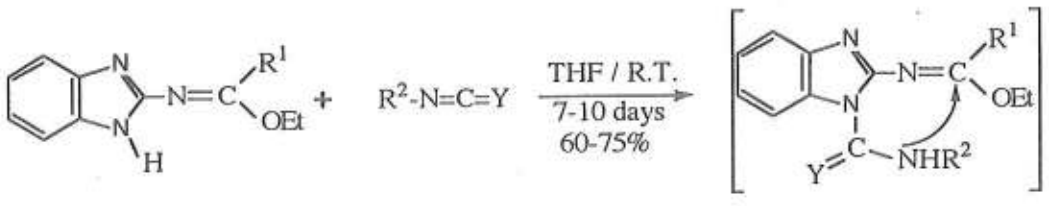
Résumé :

L'imidate N-(2-benzimidazoyl) du type 1 réagit avec les isocyanates et thioisocyanates pour conduire respectivement aux [1, 2-a] benzimidazo 1,3,5-triazin-4-one et aux [1, 2-a] benzimidazo-1,3,5-triazin-4-thione avec des rendements variant de 60-75 % .

Abstract :

N-(2-benzimidazoyl) imidate type 1 react with isocyanates and isothiocyanates to give the corresponding [1, 2-a] benzimidazo-1,3,5-triazin-4-one and [1, 2-a] benzimidazo-1,3,5-triazin-4-thione in 60-75 % overall yield .

Considerable attention has been attached to the chemistry of triazino-benzimidazole. Its derivatives have been claimed to be effective as herbicides[1] pesticides, and plant growth regulators[2]. In continuation with our studies with imidates[3-11] we report in this paper a series of triazino-benzimidazoles 3 prepared by the addition of imidates type 1 to isocyanates and isothiocyanates (Scheme 1) .



1

2

3

3	R^1	R^2	Y
3a	Me	n.Bu	O
3b	Me	Naphtyl	O
3c	Et	Naphtyl	O
3d	Me	Ph	S
3e	Me	Ph -CH_2	S
3f	Et	Ph	S
3g	Et	Ph-CH_2	S
3h	Me	Allyl	S

Scheme 1

From a mechanistic viewpoint, we may consider that the cyclization process occurs throught the formation of intermediate 2 in situ . The attack of the central carbon atom of the isocyanate or the isothiocyanate by the nitrogen atom of imidate 1 forms intermediate 2. The latter undergoes intramolecular nucleophilic cyclisation to give the corresponding [1, 2-a] benzimidazo 1,3,5-triazin –4– ones or [1, 2-a] benzimidazo 1,3,5-triazin-4-thiones 3 in moderate yields (scheme 1).

Experimental :

-Ir spectra were run in a $CHCl_3$ on a Perkin-Elmer 281 spectrometer.

-Proton NMR spectra were determined at ambient temperature with a Jeol 60 MHz spectrometer using $CDCl_3$ containing TMS as an internal standard.

-Melting points were obtained using a Büchi melting point apparatus.

-Elemental analysis was realized in the Elemental Analysis Center of Paul Sabatier University of Toulouse, France.

Imidates type 1 were prepared by the reaction of 2-aminobenzimidazole with orthoester according to publisched procedure[12,13]; all other reagents were commercially available (Aldrich Chemical Co) THF was dried and distilled on Na/ Naphtalene before use .

-General procedure for the preparation of [1,2-a] benzimidazo-1,3,5-triazin -4-one and [1, 2-a] benzimidazo-1,3,5-triazin -4- thione.

To a solution of imidate 1 (10 mmol) in dry THF (10 ml) was added isocyanate or isothiocyanate(10 mmol). The mixture was left at room temperature until a solid precipitated out (7-10 days). The product was further purified by several recrystallizations from methanol.

3a : Yield : 60 %. mp =130° C. ^{1}H NMR δ(ppm): 1.1 (t, 3H); 2,6 (s, 3H); 4.1 (t, 2H); 1.1-2 (m, 4H); 7.5-8.3 (m, 4H). Ir (cm^{-1}): $\nu_{C=O}$ = 1730; $\nu_{C=N}$ = 1625. Anal. calcd. C 65.62; H 6.25; N 21.87. Found: C 65.90; H 6.30; N 22.10.

3b : Yield : 65 %. mp =225°C. ^{1}H NMR δ(ppm): 2.2 (s, 3H); 7.5-8 (m, 11H). Ir (cm^{-1}): $\nu_{C=O}$ = 1740; $\nu_{C=N}$ = 1630. Anal. calcd. C 73.61 ; H 4.29 ; N 17.17 . Found : C 73.40 ; H 4.23; N 17.17 .

3c : Yield : 60%. mp =175°C. ^{1}H NMR δ (ppm) : 1.3 (t, 3H); 3.7 (q, 2H); 7.5-8.5 (m,11H). Ir (cm^{-1}) : $\nu_{C=O}$ = 1740; $\nu_{C=N}$ = 1630. Anal. calcd. C 74.10; H 4.70 ; N 16.47. Found : C 73.96 ; H 4.71 ; N 16.59 .

3d : Yield : 72%. mp =190°C. ^{1}H NMR δ(ppm) : 2.3(s, 3H) ; 7.5-8 (m, 9H). Ir (cm^{-1}) : $\nu_{C=N}$ = 1625

3e : Yield: 72%. mp =178°C. ^{1}H NMR δ(ppm): 2.7 (s, 3H); 6.0(s, 2H); 7.3-9.0 (m, 9H) . Ir (cm^{-1}) : $\nu_{C=N}$ = 1625. Anal. calcd. C 66.60; H 4.57 ; N 18.30. Found : C 66.58 ; H 4.53 ; N 18,40.

3e : Yield: 72%. mp =178°C. ^{1}H NMR δ(ppm): 2.7 (s, 3H); 6.0(s, 2H); 7.3-9.0 (m, 9H) . Ir (cm^{-1}) : $\nu_{C=N}$ = 1625. Anal. calcd. C 66.60; H 4.57 ; N 18.30. Found : C 66.58 ; H 4.53 ; N 18,40.

3f : Yield : 65%. mp =130°C. ^{1}H NMR δ(ppm) : 1.2 (t, 3H) ; 2.5(q, 2H); 7.5-9.0(m, 9H). Ir (cm^{-1}) : $\nu_{C=N}$ = 1625.

3g: Yield : 75%. mp =155°C. ^{1}H NMR δ (ppm): 1.4 (t, 3H); 2.9(q, 2H); 6.0(s, 2H); 7.5-9.0(m, 9H). Ir (cm^{-1}) : $\nu_{C=N}$ = 1625. Anal. calcd. C 67.5; H 5.00; N 17.50. Found : C 67.82 ; H 5.06 ; N 17.63.

3h : Yield : 75%. mp =117°C. ^{1}H NMR δ(ppm): 2.7(s, 3H); 5-5.5(m, 4H); 6 (m, 1H) ; 7.5-9.1(m, 4H) . Ir (cm^{-1}) : $\nu_{C=N}$ = 1625.

Acknowledgement: We thank Doctor A. Chihi for his helpful and discussions.

References

1. Ward Carl E,Berthold Robert V-J.Agric.Food. chem.1986, 34, 1005-10 .
2. Tesche Manfred et Coll.- Ger (East) DD 236,249 (Cl.AOIN43/90).
3. Kossai R.; Tallec A.; Hajjem B.; Baccar B.: Electrochemica Acta, 1991, 36(13), 2019 .
4. Kaddachi M.T.; Hajjem B.; Baccar, B.; J. Soc. Chim. Tunisie, 1988, 2 ,7.
5. Kaddachi M.T.; Hajjem B.; Baccar, B.; J. Soc. Chim. Tunisie, 1989, 2, 9.
6. Kaddachi M.T ; Hajjem B.; Baccar, B.; J. Soc. Chim. Tunisie, 1985, 2 , 2.
7. Hajjem B.; Chihi A.; Baccar B.; Synth. Commun. 1992, 22, 295.
8. Bellassoued M.; Gaudemar M.; Hajjem B.; Baccar B.; Bull. Soc. Chim. Belge, 1986, 95, 65.
9. Hajjem B.; Baccar B.: Synth. Commun. 1991, 21, 1501.
10. El Efrit M. L.; Hajjem B.; Baccar B.: J. Soc. Chim. Tunisie, 1990, 2 , 3-9.
11. El-Efrit M. L.; Hajjem B. and Baccar B.; J. Soc. Chim.Tunisie, 1985, 2,23.
12. Claisen L.; Ann. Chem. 1895, 287, 360 .
13. Roberts R. M.: J. Am. Chem. Soc., 1949, 71 , 3848 .