

Synthesis Morpholine Diamide By Curing Some Aromatic Hetrocyclic Primary Amines with Morpholione Phthaloyl Chloride

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Abstract

Acid chloride morpholine benzamide was prepared by react morpholine with phthalic acid anhydride to give (2-carboxy morpholine benzamide) and the following step was treatment with thionyl chloride. New ten diamide such as morpholine benz-1,2-diamide, N-substituted hetrocyclic compound were synthesized from reaction of acid chloride morpholine benzamide with various hetrocyclic primary amines. All new compounds were studied by IR spectroscopy and elemental analysis; also the physical properties of the types diamide were measured such as melting point and yield percent.

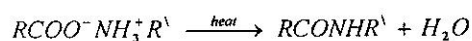
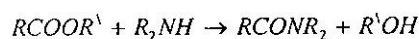
Introduction

The reaction of primary aliphatic or aromatic amines with different acid anhydrides produced amic acids, which react with thionyl chloride to give amic acid chlorides^(1,2). Amic acids, amic amides and their related derivatives have long been known to possess herbicidal activity. Derivatives of N-arylphthal amic acid, possess growth regulating properties⁽³⁻⁴⁾. Substituted amides and ureas (diamide) are another group of herbicides. Examples include the anilide such as 3, 4-dichloro phenyl ethyl amide (propanil) and 3-chloro-4-methylphenyl-1-methyl butyl amide (solan), which are extensively used for selective post-emergence weed control in rice fields⁽⁵⁾. Many main routes have been used to prepare amide compounds^(6, 7, and 8).

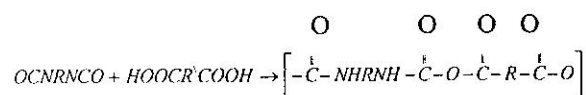
- Acid halide-amine condensation⁽⁶⁾



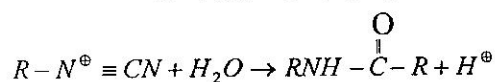
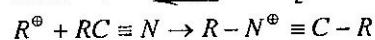
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From diisocyanate with dicarboxylic acid



* Addition Alcohol to nitrile by using acid catalyst^(7, 8)



Experimental

Melting point were recorded with Gallenhamp Melting point Apparatus and were uncorrected. IR spectra were recorded with pye unicam Sp-300 infrared spectrophotometer in KBr and Elemental analysis were carried out in the Depart of Chemistry, College of Science, University of Mosul.

Preparation of 2-Carboxy morpholine benzamide⁽⁹⁾ (I)

A mixture of (0.02)mole of phthalic anhydride and (0.02)mole of morpholine in (25)ml of dioxane was refluxed for 2hr. The product was filtered and purified by recrystallization from ethanol to give 2-carboxy morpholine benzamide in 80% yield, *m.p*185^oc, elemental analysis (found C 61.37, H 5.51, N 6.2 [C₁₂H₁₃No₄] requires C 61.27, H 5.53, N 5.95).

IR absorptions (cm⁻¹) by KBr disk: O–H str.3280, C=O str.1705 (carboxylic acid), C=O str.(amide) 1685 C–H str.3010 (aromatic), C–H str.2820 (aliphatic) C=C str.1600, 1510, 1430 (aromatic), C–N str.1380, C–O–C Str. 1120 (ether).

Preparation of 2-(Formyl Chloride) morpholine benzamide (II)

In a 100ml round bottom flask equipped with a double surface condenser fitted with anhydrous calcium chloride guard tube was placed a mixture of (0.02)mole of 2-carboxy morpholine benzamide and (0.02)mole of thionyl chloride and (25)ml of anhydrous ether. The reaction mixture was refluxed in water bath for 1hr. The solvent and excess thionyl chloride were evaporated and the resulting solid was recrystallized from dry ether, and dried in vacuum at ambient temperature to give colorless crystals of 2-(formyl chloride) morpholine benzamide in 85% yield, *m.p*193^oc elemental analysis (found C 56.77, H 4.75, N 5.29, C₁₂H₁₂NO₃Cl requires C56.8, H 4.73, N 5.52, IR absorption (cm⁻¹) by KBr disk: C=O str.1700 (amide), C=O str.1850 (acid chloride), C–H str.3080 (aromatic), C–H str.2820 (aliphatic), C=C str.1610, 1490, 1420 (aromatic), C–Cl 735.

Preparation of Morpholine Benz-1, 2-Diamide Substituted

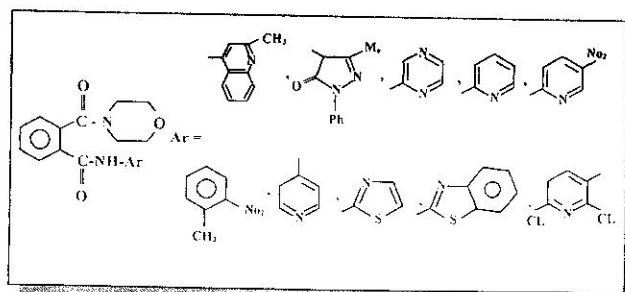
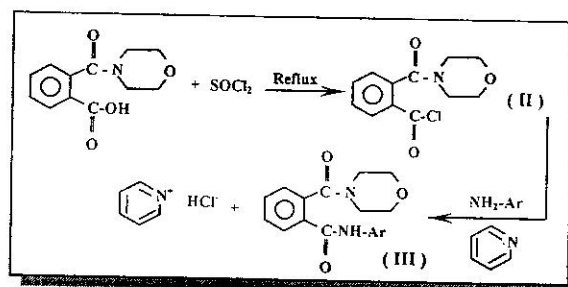
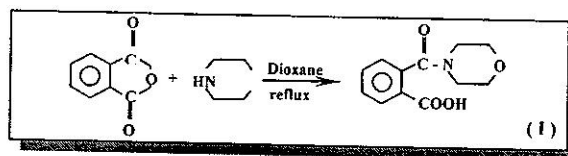
In a 100ml round bottom flask equipped with a double surface condenser fitted with anhydrous calcium chloride guard tube was placed a mixture of (0.02)mole 2-(formyl chloride) morpholine benzamid and (0.02)mole of 4-amino-2-methyl quinoline in (25)ml of dry dioxane and few drops from pyridine. The mixture was refluxed for 2hr.

Then left to cool at room temperature and poured into solution of 5% NaHCO₃, where by a crystalline solid separated out. The solid was filtered and recrystallized from ethanol.

Following the same procedure, a number of other heterocyclic primary amines were prepared. The diamides were identified by their melting point, %yields, elemental analysis and IR spectra, shown in Tables (1), (2) and (3).

Discussion

In the present paper, the reaction of 2-(Formyl chloride) morpholine benzamide with different aromatic heterocyclic primary amines to give the corresponding diamides is reported.



The reaction of 2-carboxy morpholine benzamide with thionyl chloride is carried out in anhydrous ether, and is followed by

disappearance of (O–H) absorption band at 3280cm^{-1} in the IR spectrum of the 2–(formyl chloride) morpholine benzamide and appearance of (C–Cl) absorption band of 735cm^{-1} plus their important absorption bands.

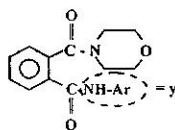
The reaction of 2–(Formyl chloride) morpholine benzamide with aromatic heterocyclic primary amines is carried out in anhydrous dioxane and is followed by disappearance of (C–CL) absorption band of 735cm^{-1} in the IR spectrum of the formyl chloride and the appearance of (C=O) absorption band at region $(1650\text{--}1755)\text{cm}^{-1}$ due to types of carbonyl group for amide and (C–N) absorption band at $(1360\text{--}1420)\text{cm}^{-1}$ in the IR spectrum of diamides.

All physical properties and elemental analysis and IR spectra for prepared diamides are listed in tables (1, 2, and 3).

The mechanism of the nucleophilic substitution of 2–(formyl chloride) morpholine benzamide with primary amines is similar to the mechanism of acetylation of amines.

Table 1

All physical properties for prepared aromatic heterocyclic amides



No. Comp.	Name	Ar	Melting Point	m.p. °C	Yield	Reag. molar	Colour
1	Morpholine benzamide		130	130	90%	Ethanol	White
2	Morpholine benzamide		130	130	90%	Ethanol	White
3	Morpholine benzamide		130	130	90%	Ethanol	White
4	Morpholine benzamide		130	130	90%	Ethanol	White
5	Morpholine benzamide		130	130	90%	Ethanol	White
6	Morpholine benzamide		130	130	90%	Ethanol	White
7	Morpholine benzamide		130	130	90%	Ethanol	White
8	Morpholine benzamide		130	130	90%	Ethanol	White
9	Morpholine benzamide		130	130	90%	Ethanol	White
10	Morpholine benzamide		130	130	90%	Ethanol	White

Table 2

Elemental analysis for morpholin derivatives

No. Comp.	Calculate			Found		
	C	H	N	C	H	N
I	61.27	5.53	5.95	61.37	5.51	6.20
II	56.8	4.73	5.52	56.77	4.75	5.29
1	67.21	4.50	13.98	67.69	4.79	14.28
4	60.99	4.89	17.43*	61.33	5.09	17.69
6	61.37	5.25	11.37	61.54	5.08	11.28
9	61.72	4.19	11.19	61.96	4.54	11.31

Table 3

Major IR Absorptions, cm^{-1} for prepared diamides

No. Comp.	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$ amide	C–C aromatic	C–H aromatic	$\nu_{\text{C-H}}$ aliphatic	$\nu_{\text{C-N}}$	$\nu_{\text{C-O-C}}$	Others
I	3280	—	1705 (acid) 1685 (amide)	1600 1510 1430	3010	2820	1380	1180	
II	—	—	1850 O (E.a.) 1700	1610 1490 1420	3080	2820	1390	1180	C–Cl 753
1.	—	3355	1740 1680	1600 1550 1490	3005	2820	1360 1390	1205	
2.	—	3340	1755 1700	1600 1590 1495	3000	(CH ₂) = 2790 (CH) = 2900	1380 1410	1220	
3.	—	3340	1740 1690	1620 1560 1490	3010	2850	1380 1410	1220	
4.	—	3335	1745 1690	1595 1550 1490	3010	2890	1375 1390	1260	
5.	—	3340	1700 1650	1630 1600 1550	3080	2920	1370 1395	1245	
6.	—	3360	1720 1690	1600 1520 1490	3100	2920 2880	1385 1400	1260	
7.	—	3354	1760 1700	1600 1590 1500	3020	2900	1360 1410	1260	
8.	—	3290	1780 1685	1620 1560 1480	3090 3120	2895	1380 1420	1240	
9.	—	3340	1700 1695	1600 1570 1490	3050 3100	2910	1390 1420	1220	
10.	—	3340	1730 1690	1610 1590 1480	3070	2900	1380 1410	1260	C–Cl 745

References

- Ahmed, Shihab Ahmed, (1992) "Synthesis of Poly [N–substituted Maleimides] and Copolymerization with Vinyl acetate with the prepared N–substituted Maleimides". Ph.D.Thesis, Univ. of Baghdad–Iraq.
- Barzangi, Azad S.S. (1999) "Grafting phenols formaldehyde Resins with some Unsaturated Amic Acids, their imides

3. Matcalf, R.L, (1971) "The Chemistry and Biology of Pesticides" in Pesticides in the Environment, White–Steven, R, Decker, New York 1:1.
4. Matcalf, R.L, (1974) "Pesticides Manual" (Eds. Martin. H. and worthing, C.R. 4th, Ed., British Crop. Protection Council.
5. Cremlyn, R. (1979) "Pesticides, Preparation and Mode of Action " , John-Wiley and Sons, Chap. 8.
6. Harms,D.H. (1953) "Determination of Some Chlorine–Substituted Methanes and Ethanes" Anal, Chem., 25:140.
7. Nortonder, D. (1894) "Synthesis of Amides from Nitriles" Ann., 280:167.
8. Kulicke,W.M. R. Kniewske, and J. Klenn (1982) "The Chemistry of Amides" Prog. Polym, sci. 8:373.
9. Heravi , M.M., R.H. Shoar and L. Perdram, (2005) "Synthesis of N-Arylphthalimides Catalyzed By 1,4–Diazabicyclo [2, 2, 2] Octane" J. of Molecular Catalysss A: chemical, 231:89–91,.

تحضير ثنائي اميد المورفولين بمعاملته ببعض الامينات الاولية الاروماتية غير المتجانسة مع كلوريد فنالويل مورفولين

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الخلاصة

تم مفاعلة المورفولين مع حامض الفثاليك اللامائي الذي فوعل مع كلوريد الثايونيل للحصول على المركب (2-Formyl chloride) morpholine benzamide) وبمعاملة كلوريد الحامض الجديد مع امينات حلقيه غير متجانسة مختلفة تكونت عشر مركبات جديدة من نوع (Morpholine benzamide N-hetrocyclic) تم تشخيص هذه المركبات فيزيائياً وطيفياً عن طريق درجات الانصهار وطيف الـ IR والتحليل الدقيق للعناصر C, H, N.