

SYNTHESIS OF SOME TEREPHTHALO-N,N'-DI AND TETRA SUBSTITUTED AMIDOXIMES

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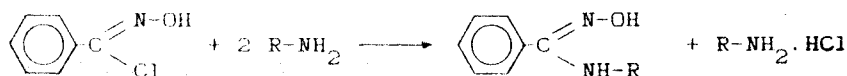
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ABSTRACT

In this work, the reactions of some primary and secondary amines with terephthalohydroxymoyl chloride and the properties of these products were studied.

INTRODUCTION

N-mono alkyl or aryl substituted and N, N'-disubstituted amidoximes are the derivatives of the amidoximes. There are many methods to the synthesis of N-substituted amidoximes (Eloy, 1962). Generally, they are prepared from the hydroximic acid chlorides and amines.



Benzhydroximoyl chloride

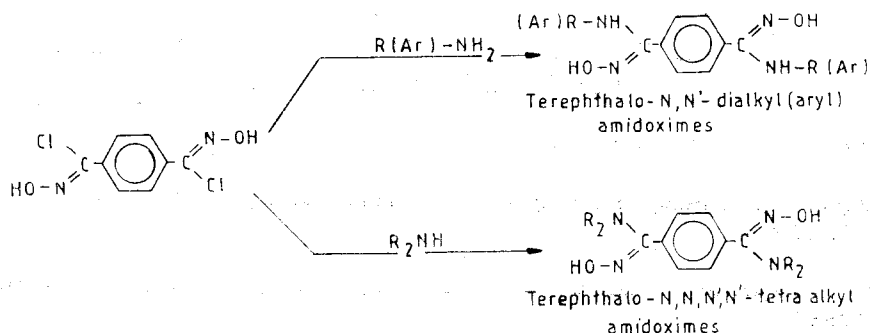
N-alkyl benzamidoxime

Amidoximes and their N-substituted derivatives are amphoteric substances (Eloy, 1962 a). The -NH₂ group in the amidoximes is the basic, and N-OH is acidic group. Amidoximes and also N-substituted amidoximes show tautomeric properties (Smith, 1966a). However, oxime form is more dominated than imine form.

EXPERIMENTAL

Terephthalo -N,N'- dialkyl (or aryl) amidoximes and terephthalo -N, N, N, N'- tetra alkyl amidoximes were obtained from the reactions

of the primary and secondary amines with terephthalohydroximoyl chloride.



R: CH_3CH_2 -; HOCH_2CH_2 -; $\text{C}_6\text{H}_5\text{-CH}_2$ -; α -Furfuryl; HOOC-CH_2 -

Ar: C_6H_5 -; $p\text{-CH}_3\text{-C}_6\text{H}_4$ -; α -Naphthyl; $p\text{-Br-C}_6\text{H}_4$ -

R₂: $(\text{CH}_3)_2$; $(\text{CH}_3\text{CH}_2)_2$; $(\text{C}_6\text{H}_5\text{-CH}_2)_2$; $(\text{C}_6\text{H}_5)_2$; $(\text{HO-CH}_2\text{CH}_2)_2$;

All chemicals used are commercial and pure grade. Terephthalohydroximoyl chloride was synthesized from the terephthalaldehyde (Rheinboldt, 1926; Ricca, 1961; Karataş, 1989).

Elemental analysis, NMR spectrophotometer (Varian 60-A), IR spectrophotometer (Pye-Unicam SP-1025) and Melting Point (Buchi SPM-20) data were used to elucidate the structure of the products.

General Procedure:

In a flask, 4 mmol (0.932 g) terephthalohydroximoyl chloride was dissolved in the approximately 30 ml of ethyl alcohol and then was placed in a salt-ice bath at -10 – 0°C . The solution of the 9 mmol primary or secondary amines in 20 ml ethyl alcohol was added slowly by stirring into the flask. After a few minutes or a few hours, precipitation commenced depending on the base strength of the amines. However, some experiments were run under the refluxing of ethyl alcohol. After the reaction is completed, the mixture was diluted with water, and was filtered, washed with water and ethyl alcohol, and dried under vacuum, then recrystallized. Elemental analysis, spectral data (These data are very well consistent with the values of Navech, 1957 for amidoximes), and physical properties were given in the Table-I and Table-II.

Table 1. Some physical properties of terephthalo -N,N²- di (or tetra) alkyl amidoximes.

R	R'	React. Temp. (°C)	React. Time (min.)	Yield (%)	m.p. (°C)	Solubility
H	CH ₃ -CH ₂ -	-10	20	89	227-9	Ethanol-σ Dioxane-σ
H	HOCH ₂ CH ₂ -	-10	30	78	220-2	Ethanol-σ Pyridine-s
H	C ₆ H ₅ CH ₂ -	-10	30	82	192-4	Ethanol-σ Dioxane-s
H	α-Furfuryl	-5	30	82	201-2	Ethanol-σ Dioxane-v
H	p-CH ₃ -C ₆ H ₄ -	0	30	79	234-5	Ethanol-σ Dioxane-v
H	C ₅ H ₅ -	0	90	83	208-10	Ethanol-σ Dioxane-v
H	α-naphthyl	0	120	67	214-6	Pyridine-s Dioxane-v
H	p-Br-C ₆ H ₄ -	76-78	120	65	219-21	Ethanol-s Dioxane-v
CH ₃ -	CH ₃ -	-10	20	83	190-1	Ethanol-σ Dioxane-v
CH ₃ CH ₂ -	CH ₃ CH ₂ -	-10	20	84	172-4	Ethanol-s Dioxane-v
C ₆ H ₅ CH ₂ -	C ₆ H ₅ CH ₂ -	-10	20	67	180-2	Ethanol-σ Dioxane-v

RESULTS AND DISCUSSION

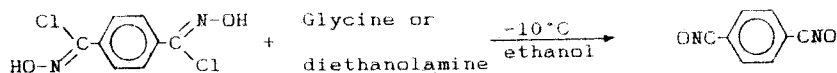
The reactions of terephthalohydroximoyl chloride with amines were not found in the literature. Eloy (1964) reported that R-HN (HO-N) C-C₆H₄-C (N-OH) NH-R structure was formed with the reaction of amines and terephthalodinitrile oxide obtained from terephthalohydroximoyl chloride.

A number of amines gave the substitution products with terephthalohydroximoyl chloride but glycine, diethanolamine and diphenylamino do not gave the expected product. No product is formed with the diphenyl amine; glycine and diethanolamine gave rapid reaction but the products were not terephthalo-N,N²-di (or tetra) alkyl amidoxime, they identified as terephthalodinitrile oxide. [NMR (δ): arom: C-H 8,45 ppm; IR (γ): N-O⁻ 1110, C≡N 2320 cm⁻¹]. These results are same with presented literatures (Smith, 1966).

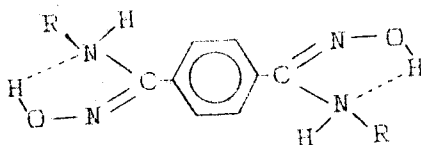
Table 2. Analytical results of terephthalo-N, N'- di (or tetra) alkyl amidoximes.



Compound		Found (%) (Calc.)			NMR (δ) (ppm)	IR (cm^{-1})
R	R'	C	H	N		
H	CH ₃ CH ₂ -	57.59 (57,58)	6.90 (7,25)	21.9 (22,38)	1.05 (t, -CH ₃) 3.30 (q, -CH ₂ -) 5.50 (s, -NH-) 7.85 (m, -CH arom.) 10.20 (s, N-OH)	910- 950 N—O 1660 C=N 3150-3250 O—H and NH
H	HOCH ₂ CH ₂ -	51.59 (51,06)	6.37 (6,43)	19.77 (19,85)	3.10 (t, -CH ₂ CH ₂ -) 4.80 (s, -NH-) 6.00 (t, C-OH) 7.80 (c, -CH arom.) 10.25 (s, N-OH)	910- 960 N—O 1655 C=N 3200-3300 O—H and NH
H	zfurfuryl	59.95 (61,01)	4.99 (5,12)	15.89 (15,81)	4.30 (d, -CH ₂) 6.20 (t, -CH. furan) 6.60 (t, -NH-) 7.85 (s, -CH arom.) 10.40 (s, N-OH)	930 N—O 1660 C=N 3160-3280 O—H and NH
H	C ₅ H ₅ -CH ₂ -	70.03 (70,57)	5.91 (5,92)	14.88 (14,96)	4.20 (d, -CH ₂ -) 6.35 (t, -NH-) 7.1-7.3 (m, -CH arom.) 9.95 (s, N-OH)	930 N—O 1650 C=N 3220-3350 O—H and NH
H	C ₆ H ₅ -	70.08 (69,35)	5.14 (5,24)	16.11 (16,18)	6.9-7.4 (m, -CH arom.) 8.70 (s, -NH-)	920-950 N—O 1610-1650 C=N
H	p-CH ₃ - -C ₆ H ₄ -	71.02 (70,57)	5.88 (5,92)	14.57 (14,96)	11.10 (s, N-OH) 2.10 (s, -CH ₃) 6.8-7.6 (m, -CH arom.)	3100-3250 O—H and NH 910-950 N—O 1640 C=N
H	p-Br-C ₆ H ₄ -	48.10 (47,64)	3.36 (3,20)	11.08 (11,11)	8.4 (s, -NH-) 11.0 (s, N-OH) 6.7-7.4 (m, -CH arom.)	3150-3250 O—H and NH 910- 950 N—O
	α-naphthyl-	74.88 (75,32)	4.96 (4,97)	11.97 (12,55)	8.8 (s, -NH-) 11.15 (s, N-OH) 6.8-7.4 (m, -CH arom.)	1630-1650 C=N 3240-3280 O—H and NH 940 N—O
CH ₃ -	CH ₃ -	57.96 (57,58)	7.15 (7,25)	22.02 (22,38)	8.4 (s, -NH-) 11.10 (s, -NO-H) 1.0 (d, -CH ₃) 7.80 (m, -CH arom.)	3220-3280 O—H and NH 910- 980 N—O 1645 C=N
CH ₃ CH ₂ -	CH ₃ CH ₂ -	62.59 (62,67)	8.15 (8,55)	17.90 (18,28)	10.6 (s, N-OH) 1.05 (t, -CH ₃) 3.30 (q, -CH ₂ -) 7.85 (s, -CH arom.)	3250-3320 O—H and NH 900- 940 N—O 1640 C=N
C ₆ H ₅ CH ₂ -	C ₆ H ₅ CH ₂ -	77.35 (77,95)	6.23 (6,18)	9.90 (10,10)	10.45 (s, N-OH) 4.10 (m, -CH ₂ -) 7.70 (s, -CH arom.) 10.40 (s, N-OH)	3250-3330 O—H and NH 920 N—O 1620-1660 C=N 3250-3300 O—H and NH



The NMR and IR values are in accordance with the amidoximes. 3400 cm^{-1} IR value indicates that there is intramolecular hydrogen bond in the molecules, as shown below:



As a result, 8 new terephthalo- N,N^2 -di alkyl (or aryl) amidoximes and 3 new terephthalo- $\text{N},\text{N},\text{N}^2,\text{N}^2$ -tetra alkyl amidoximes were synthesized and it is proved that glycine and diethanolamine may be used just as tertiary amines to obtain terephthalodinitrile oxide from terephthalohydroximoyl chloride.

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