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NOTE

Ultrasound-Assisted Synthesis and Biological Activity of Oximes

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The conversion of alicyclic, aliphatic carbonyl compounds and aromatic aldehydes into the corresponding oximes was achieved by ultrasound irradiation in presence of hydroxylamine hydrochloride and potassium carbonate. The biological test showed that the synthesized compound has weak fungicidal activity. The structures of compounds were characterized by melting points, ^{1}H NMR and IR.

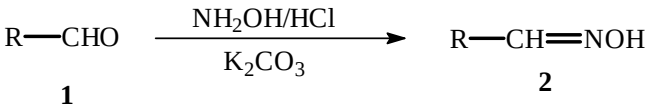
Key Words: Ultrasound irradiation, Oximes, Biological activity.

Several functional group transformations of oximes make them very important in synthetic organic chemistry. Among other synthesis applications, these compounds not only represent a convenient series of derivatives of carbonyl compounds but may be used as intermediates for the preparation of amides by the Beckmann rearrangement[1], nitrones[2], hydroximinoyl chlorides[3], nitrile oxide[3] and chiral a-sulfinyl oximes[4]. Therefore, synthetic organic chemists are interested in a facilitation of oxime synthesis.

Although alternative methods exist[5] for reaction of carbonyl compounds with hydroxylamine hydrochloride remains still the most important route. The classical method involves refluxing of an alcoholic solution of these reactants in the presence of sodium acetate or hydroxide[6]. Under certain circumstances, ultrasonic irradiation can replace the heating procedure[7]. Here, the compounds were synthesized by applying ultrasound irradiation and their biological activity was tested.

Melting points were determined using a Yanaco MP-241 apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Equinox55 spectrophotometer as potassium bromide tablets. ^{1}H NMR spectra were measured on a Bruker AC-P500 instrument (300 MHz) using tetramethylsilane as an internal standard and $CDCl_3$ as solvent. Ultrasonic irradiation was carried out with KQ-218 ultrasonic cleaner 20 kHz/50 W.

The reactants in the molar ratio carbonyl compound/$NH_2OH \cdot HCl$/K_2CO_3 = 1:1.2:1.2 were dissolved in water/EtOH = 1:1 at room temperature. Then the mixture were exposed to the ultrasound (**Scheme-I**). The compound was irradiated for 10-30 min (Table-1) and the completion of the reaction is monitored by TLC examination. In the case of products the reaction mixture was carefully extracted with ether or CH_2Cl_2, the organic phase washed with H_2O, dried (Na_2SO_4) and the solvent evaporated. Yields are given in Table-1. Almost all derived oximes are known compounds and their spectral data as well as melting points of solids, were in agreement with the literature values.



1 **2**

Scheme-I

TABLE-1
PHYSICAL DATA OF OXIMES UNDER ULTRASOUND IRRADIATION

Substrate	R	Time (min)	Products	Yield (%)
1a	C_6H_5	30	2a	92.2
1b	*p*-$CH_3C_6H_4$	20	2b	78.4
1c	*p*-$OCH_3C_6H_4$	20	2c	82.1
1d	*o*-BrC_6H_4	15	2d	82.3
1e	*o*-FC_6H_4	15	2e	89.6
1f	*o*-ClC_6H_4	15	2f	90.3
1g	*m*-$NO_2C_6H_4$	15	2g	90.3
1h	*p*-$NO_2C_6H_4$	15	2h	91.6
1i	2,4-$Cl_2C_6H_3$	15	2i	84.6
1j	*p*-BrC_6H_4	15	2j	85.6
1k	*p*-OHC_6H_4	20	2k	86.9
1l	*o*-$OCH_3C_6H_3$	20	2l	88.6
1m	3,4-$(CH_3)_2C_6H_3$	20	2m	81.2
1n	3,4-$(OCH_3)_2C_6H_3$	20	2n	78.6
1o	$N(CH_3)_2C_6H_4$	10	2o	92.3

Bioassay of fungicidal activities

Fungicidal activities of the oximes against *G. zeae* Petch, *Phytophthora infestans* (Mont.) de Bary, *Botryosphaeria berengeriana* f. sp. *piricola* (Nose) koganezawa et Sakuma, *Fusarium oxysporum* f.sp. *cucumerinum* and *Cercospora arachidicola* were evaluated using the mycelium growth rate test. The culture media, with known concentration of the test compounds. The blank test was made using acetone. The culture was carried out at 24 ± 0.5ºC. Three replicates were performed.

Primary bioassay (Table-2) showed that the tested compounds has weak fungicidal activity against *G. zeae* Petch, *B. cinerea* Pers, *Phytophthora infestans* (Mont.) de Bary, *Botryosphaeria berengeriana* f. sp. *piricola* (Nose) koganezawa et Sakuma, *Fusarium oxysporum* f.sp. *cucumerinum* and *Cercospora arachidicola*. All of the results in this paper will be useful for later research.

TABLE-2
FUNGICIDAL ACTIVITY OF TESTED COMPOUNDS AT 50 ppm

Products	R	*G. zeae* Petch	*Phytophthora infestans* (Mont.) de Bary	*Botryosphaeria berengeriana* f. sp. *piricola* (Nose) koganezawa et Sakuma	*Fusarium oxysporum* f.sp. *cucumerinum*	*Cercospora arachidicola*
2b	*p*-$CH_3C_6H_4$	14.3	15.6	19.8	35.1	27.9
2c	*p*-$OCH_3C_6H_4$	19.0	23.1	17.6	24.4	0.0
2d	*o*-BrC_6H_4	21.3	35.8	22.5	48.9	31.2
2e	*o*-FC_6H_4	45.6	70.1	41.2	20.1	38.6
2f	*o*-ClC_6H_4	38.1	65.4	41.2	68.9	42.8
2g	*m*-$NO_2C_6H_4$	20.2	17.1	25.6	33.8	12.3
2h	*p*-$NO_2C_6H_4$	0.0	23.1	23.5	46.7	21.4
2i	2,4-$Cl_2C_6H_3$	43.2	21.3	29.8	18.9	16.3
2j	*p*-BrC_6H_4	38.1	69.2	35.3	64.4	39.3
2k	*p*-OHC_6H_4	0.0	23.1	23.5	20.0	21.4
2l	*o*-$OCH_3C_6H_3$	17.9	15.9	18.4	23.5	25.4
2m	3,4-$(CH_3)_2C_6H_3$	19.8	14.6	32.3	16.7	42.4
2n	3,4-$(OCH_3)_2C_6H_3$	36.9	18.7	29.8	15.8	19.8
2o	$N(CH_3)_2C_6H_4$	34.3	24.5	28.3	66.4	24.1

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