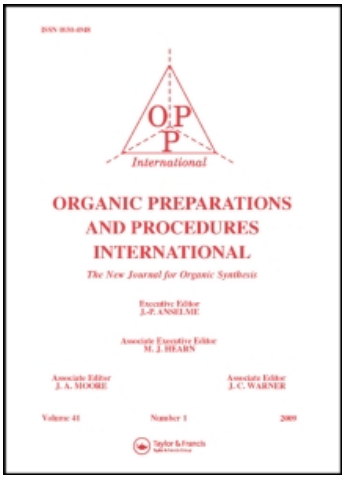

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NOVEL STEREOSELECTIVE SYNTHESIS OF *E*- ARYL ALDOXIME AND KETOXIME O-ETHERS

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NOVEL STEREOSELECTIVE SYNTHESIS OF *E*-ARYL ALDOXIME AND KETOXIME O-ETHERS

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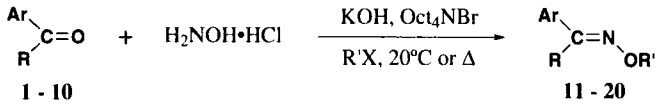
Aldoxime and ketoxime O-ethers, especially heteroaromatic ones, exhibit a wide spectrum of biological activity.[1] The known methods for the synthesis of oxime O-ethers are based on alkylation of oximes salts (NaH/DMF[2] or alkali alkoxides[3-5]) with alkyl halides (mainly bromides or iodides), as well as by condensation of carbonyl compounds with O-alkylhydroxylamines.[1a] The possibility of carrying out alkylation of oximes in the presence of phase transfer catalysis (PTC) systems 10% aq. NaOH/C_6H_6/R_4NX (R = *n*-Bu, *n*-Oct; X = Br, HSO_4)[6-9] or solid K_2CO_3 / C_6H_6 / 18-crown-6[10] considerably simplifies these alkylation reactions. Recently we developed two novel PTC methods for preparation of aromatic and heteroaromatic ketoxime O-ethers both from the ketoximes and alkyl iodides prepared *in situ* from alkyl chlorides[11] and ketoxime O-acetates and benzoates.[12] However, the stereoselectivity in oxime O-ether synthesis is usually not high. We now report a simple one-pot PTC synthesis of aryl and heteroaryl aldoxime and ketoxime O-ethers **11-20** directly from corresponding carbonyl compounds **1-10**.

The process involves the formation of the corresponding oxime K-salts which then undergo alkylation with alkyl and propargyl halides (*Table 1*). Exploratory experiments showed that highly lipophilic tetraoctylammonium bromide, located almost completely in organic phase, was the most effective catalyst. The other ammonium salts studied (Bu_4NBr, $PhCH_2Bu_3NCl$) were fairly effective in the synthesis of oxime ethers, whereas the crown ethers (15-crown-5 and 18-crown-6) were substantially less active.[8] The formation of oxime O-ethers usually was stereoselective - in most cases the E-isomers being isolated as single products. Low stereoselectivity was obtained only in the synthesis of thiophene containing aldoxime and ketoxime O-ethers **15,16a-c**.

The products were purified by column chromatography in 40-79% yields. Unfortunately, the desired products were not obtained in two cases with pyridine containing oxime ethers **18a** and **20a** because of side-reactions (quaternization) in the presence of MeI. Similar reasons caused also low yields of products **17a** and **19a** (17%). The structure of obtained O-ethers **11-20** was confirmed by ^1H NMR spectroscopy. [13]



1 - 10 11 - 20

TABLE 1. Synthesis of Oxime O-ethers from Carbonyl Compounds under PTC Conditions

Ar	R	R'X	Product	E/Z	Time (h)	Yield (%)	Liter. bp./mm Hg(mp.) (°C)
Ph	H	MeI	**11a**	100:0	3	47	95-96/20[14]
Ph	H	EtBr	**11b**	100:0	3	52	98/ 8[14]
Ph	H	HC≡CCH$_2$Br	**11c**	100:0	3	79	(- - -)[15]
Ph	Me	MeI	**12a**	100:0	6	39	(- - -)[16]
Ph	Me	EtBr	**12b**[a]	100:0	2	56	
Ph	Me	HC≡CCH$_2$Br	**12c**	100:0	3	57	(- - -)[17]
2-Furyl	H	MeI	**13a**	96:4	4	32	(- - -)[18]
2-Furyl	H	EtBr	**13b**[a]	100:0	4	49	
2-Furyl	H	HC≡CCH$_2$Br	**13c**	98:2	2	42	64-65/0.4[15]
2-Furyl	Me	MeI	**14a**[a]	92:8	3	40	
2-Furyl	Me	EtBr	**14b**[a]	91:9	3	49	
2-Furyl	Me	HC≡CCH$_2$Br	**14c**	100:0	3	74	105-106/10[10]
2-Thienyl	H	MeI	**15a**[a]	80:20	2	42	
2-Thienyl	H	EtBr	**15b**[a]	75:25	2	65	
2-Thienyl	H	HC≡CCH$_2$Br	**15c**[a]	87:13	2	47	
2-Thienyl	Me	MeI	**16a**	58:42	9	42	(- - -)[12]
2-Thienyl	Me	EtBr	**16b**[a]	62:38	6	50	
2-Thienyl	Me	HC≡CCH$_2$Br	**16c**	69:31	4	56	125-128/10[10]
3-Pyridyl	H	MeI	**17a**	100:0	2	17	100-101/17[4]
3-Pyridyl	H	EtBr	**17b**	100:0	3	34	160-161(HCl salt)[19]
3-Pyridyl	H	HC≡CCH$_2$Br	**17c**	100:0	2	41	(55)[20]
3-Pyridyl	Me	EtBr	**18b**[a]	100:0	4	43	
3-Pyridyl	Me	HC≡CCH$_2$Br	**18c**[a]	100:0	4	50	
4-Pyridyl	H	MeI	**19a**	100:0	2	17	56/0.012[19]
4-Pyridyl	H	EtBr	**19b**	100:0	4	50	48-49/0.05[4]
4-Pyridyl	H	HC≡CCH$_2$Br	**19c**	100:0	2	43	(84.5-85) (N-oxide)[19]
4-Pyridyl	Me	EtBr	**20b**[a]	100:0	6	43	
4-Pyridyl	Me	HC≡CCH$_2$Br	**20c**[a]	100:0	3	46	

a) Correct elemental analysis could not be obtained due to volatility of products (Carlo Erba, mod. 1108 apparatus)

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on a Bruker WH/DS (90 MHz) instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were registered on an MS-25 spectrometer (Kratos, 70 eV). GC analysis was performed on an Chrom-5 instrument equipped with flame-ionization detector using glass column packed with 5% OV-101 on Chromosorb W-HP (80-100 mesh). Carbonyl compounds **2-10**, alkyl halides and tetraoctylammonium bromide were Aldrich products. Benzaldehyde **1** and propargyl bromide were distilled prior to use.

General Procedure of the Synthesis of Aldoxime and Ketoxime O-Ethers 11-20.- To a solution of carbonyl compound (20 mmol) and tetraoctylammonium bromide (0.27 g, 0.5 mmol) in toluene (15 mL) were added powdered hydroxylamine hydrochloride (3.48 g, 25 mmol) and 25 mL of 25% aq. solution of KOH. The reaction mixture was refluxed for 2 h. The alkyl halide (80 mmol) was then added, and the reaction mixture was stirred for 2-9 h under reflux (for the preparation of propargyl ethers **11-20c** room temperature was used) (see Table). At the end of reaction the organic phase was separated, dried over anhydrous $MgSO_4$, and filtered; toluene was evaporated at reduced pressure and the residue was chromatographed on silica gel (eluent benzene for phenyl, furyl and thienyl containing oxime ethers or benzene-ethyl acetate 1:1 for pyridine containing ethers) to obtain products **11-20**.

Benzaldehyde O-Methyloxime (11a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 3.91 (s, 3H, CH_3), 7.2-7.6 (m, 5H, Ph), 7.96 (s, 1H, CH). MS *m/z*: 135 (100, M^+), 108 (21), 103 (44), 89 (7), 78 (32), 77 (79), 65 (17), 51 (36), 39 (10).

Benzaldehyde O-Ethyloxime (11b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.25 (t, 3H, J = 7.2 Hz, CH_3), 4.16 (q, 2H, J = 7.2 Hz, CH_2), 7.2-7.6 (m, 5H, Ph), 8.00 (s, 1H, CH). MS *m/z*: 149 (75, M^+), 120 (54), 104 (45), 94 (65), 89 (37), 78 (48), 77 (100), 66 (35), 65 (38), 51 (75), 39 (20).

Benzaldehyde O-Propargyloxime (11c).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.48 (t, 1H, J = 3.0 Hz, CH), 4.77 (d, 2H, J = 3.0 Hz, CH_2), 7.2-7.7 (m, 5H, Ph), 8.10 (s, 1H, CH=). MS *m/z*: 159 (40, M^+), 130 (31), 129 (82), 128 (59), 115 (13), 104 (20), 90 (44), 89 (63), 77 (82), 65 (100), 51 (71), 39 (64).

Acetophenone O-Methyloxime (12a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.18 (s, 3H, CCH_3), 3.94 (s, 3H, OCH_3), 7.2-7.7 (m, 5H, Ph). MS *m/z*: 149 (56, M^+), 118 (37), 108 (12), 103 (13), 77 (100), 51 (37).

Acetophenone O-Ethyloxime (12b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 2.18 (s, 3H, CCH_3), 4.20 (q, 2H, J =7.0 Hz, $C\underline{H}_2CH_3$), 7.2-7.9 (m, 5H, Ph). MS *m/z*: 163 (49, M^+), 134 (41), 118 (43), 106 (32), 103 (34), 94 (27), 77 (100), 66 (15), 51 (42), 43 (18).

Acetophenone O-Propargyloxime (12c).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.17 (s, 3H, CH_3), 2.40 (t, 1H, J = 2.6 Hz, CH), 4.73 (d, 2H, J = 2.6 Hz, CH_2). MS *m/z:* 173 (29, M^+), 172 (29), 144 (18), 128 (25), 116 (29), 106 (66), 103 (60), 76 (56), 77 (100), 65 (36), 51 (49), 39 (44).

2-Furancarboxaldehyde O-Methyloxime (13a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 3.87 (s, 3H, CH_3), 6.38 (m, 1H, 4-H), 6.51 (m, 1H, 3-H), 7.40 (m, 1H, 5-H), 7.82 (s, 1H, CH); (Z-

isomer): 3.96 (s, 3H, CH_3), 6.38 (m, 1H, 4-H), 6.51 (m, 1H, 3-H), 7.40 (m, 1H, 5H), 7.91 (s, 1H, CH). MS *m/z*: 125 (93, M^+), 98 (9), 94 (44), 83 (72), 79 (12), 66 (25), 55 (18), 52 (35), 39 (100).

2-Furancarboxaldehyde O-Ethyloxime (13b).- colorless liquid. ^1H NMR ($CDCl_3$): (E-isomer) δ 1.25 (t, 3H, J = 7.2 Hz, CH_3), 4.18 (q, 2H, J = 7.2 Hz, CH_2), 6.38 (m, 1H, 4-H), 6.51 (m, 1H, 3-H), 7.41 (m, 1H, 5-H), 7.89 (s, 1H, CH). MS *m/z*: 139 (60, M^+), 111 (100), 94 (40), 81 (23), 68 (66), 52 (39), 39 (95).

2-Furancarboxaldehyde O-Propargyloxime (13c).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 2.40 (t, 1H, J = 2.6 Hz, CH), 4.69 (d, 2H, J = 2.6 Hz, CH_2), 6.38 (m, 1H, 4-H), 6.55 (m, 1H, 3-H), 7.40 (m, 1H, 5-H), 7.93 (s, 1H, CH); (Z-isomer): 2.40 (t, 1H, J = 2.6 Hz, CH), 4.73 (d, 2H, J = 2.6 Hz, CH_2), 6.38 (m, 1H, 4-H), 6.55 (m, 1H, 3-H), 7.40 (m, 1H, 5-H), 8.06 (s, 1H, CH). MS *m/z*: 149 (38, M^+), 94 (30), 83 (44), 80 (75), 66 (22), 52 (80), 39 (100).

2-Acetylfuran O-Methyloxime (14a).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 2.12 (s, 3H, CCH_3), 3.91 (s, 3H, OCH_3), 6.40 (m, 1H, 4-H), 6.54 (m, 1H, 3-H), 7.41 (m, 1H, 5-H); (Z-isomer) 2.21 (s, 3H, CCH_3), 3.91 (s, 3H, OCH_3), 6.40 (m, 1H, 4-H), 7.15 (m, 1H, 3-H), 7.41 (m, 1H, 5-H). MS *m/z*: 139 (75, M^+), 108 (52), 94 (24), 83 (61), 66 (38), 53 (28), 43 (61), 39 (100).

2-Acetylfuran O-Ethyloxime (14b).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.09 (s, 3H, CCH_3), 4.20 (q, 2H, J = 7.2 Hz, $C\underline{H}_2CH_3$), 6.38 (m, 1H, 4-H), 6.58 (m, 1H, 3-H), 7.42 (m, 1H, 5-H); (Z-isomer) 1.31 (t, 3H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.21 (s, 3H, CCH_3), 4.20 (q, 2H, J = 7.2 Hz, $C\underline{H}_2CH_3$), 6.45 (m, 1H, 4-H), 7.15 (m, 1H, 3-H), 7.53 (m, 1H, 5-H). MS *m/z*: 153 (30, M^+), 125 (28), 53 (100), 39 (45).

2-Acetylfuran O-Propargyloxime (14c).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 2.13 (s, 3H, CH_3), 2.40 (t, 1H, J = 2.6 Hz, CH), 4.76 (d, 2H, J = 2.6 Hz, CH_2), 6.38 (m, 1H, 4-H), 6.60 (m, 1H, 3-H), 7.40 (m, 1H, 5-H). MS *m/z*: 163 (27), 108 (10), 94 (54), 93 (23), 83 (31), 66 (100), 53 (15), 39 (75).

2-Thiophenecarboxaldehyde O-Methyloxime (15a).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 3.89 (s, 3H, CH_3), 6.89 (m, 1H, 4-H), 7.11 (m, 1H, 5-H), 7.22 (m, 1H, 3-H), 8.16 (s, 1H, CH); (Z-isomer) 4.05 (s, 3H, CH_3), 6.89 (m, 1H, 4-H), 7.11 (m, 1H, 5-H), 7.45 (m, 1H, 3-H), 7.67 (s, 1H, CH). MS *m/z*: 141 (100, M^+), 110 (44), 99 (65), 96 (35), 70 (31), 57 (40), 43 (98), 39 (40).

2-Thiophenecarboxaldehyde O-Ethyloxime (15b).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 4.16 (q, 2H, J = 7.0 Hz, $C\underline{H}_2CH_3$), 6.96 (m, 1H, 4-H), 7.13 (m, 1H, 5-H), 7.27 (m, 1H, 3-H), 8.18 (s, 1H, CH); (Z-isomer) 1.33 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 4.33 (q, 2H, J = 7.0 Hz, $C\underline{H}_2CH_3$), 6.96 (m, 1H, 4-H), 7.13 (m, 1H, 5-H), 7.47 (m, 1H, 3-H), 7.61 (s, 1H, CH). MS *m/z*: 155 (87, M^+), 127 (85), 110 (40), 100 (30), 99 (38), 84 (100), 70 (32), 57 (29), 43 (73), 39 (60).

2-Thiophenecarboxaldehyde O-Propargyloxime (15c).- colorless liquid, ^1H NMR ($CDCl_3$): (E-isomer) δ 2.27 (t, 1H, J = 2.6 Hz, CH), 4.67 (d, 2H, J = 2.6 Hz, CH_2), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.27 (m, 1H, 3-H), 8.22 (s, 1H, CH=); (Z-isomer) 2.27 (t, 1H, J = 2.6 Hz, CH), 4.78 (d, 2H, J = 2.6 Hz, CH_2), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.51 (m, 1H, 3-H), 7.67 (s, 1H, CH=). MS *m/z*:

165 (35, M^+), 135 (9), 110 (27), 99 (70), 96 (100), 91 (10), 70 (33), 57 (15), 45 (23), 39 (53).

2-Acetylthiophene O-Methyloxime (16a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.24 (s, 3H, CCH_3), 3.91 (s, 3H, OCH_3), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.45 (m, 1H, 3-H); (Z-isomer) 2.31 (s, 3H, CCH_3), 4.00 (s, 3H, OCH_3), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.45 (m, 1H, 3-H). MS *m/z*: 155 (100, M+), 124 (68), 114 (11), 109 (29), 99 (33), 84 (18), 57 (12), 45 (22), 39 (38).

2-Acetylthiophene O-Ethyloxime (16b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.29 (t, 3H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.22 (s, 3H, CCH_3), 4.20 (q, 2H, J = 7.2 Hz, $C\underline{H}_2CH_3$), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.45 (m, 1H, 3-H); (Z-isomer) 1.34 (t, 3H, J = 7.2 Hz, $CH_2C\underline{H}_3$), 2.31 (s, 3H, CCH_3), 4.27 (q, 2H, J = 7.2 Hz, $C\underline{H}_2CH_3$), 6.98 (m, 1H, 4-H), 7.16 (m, 1H, 5-H), 7.45 (m, 1H, 3-H). MS *m/z*: 169 (100, M^+), 141 (66), 124 (64), 109 (70), 100 (34), 99 (42), 84 (54), 65 (15), 58 (23), 50 (15), 45 (24), 39 (54).

2-Acetylthiophene O-Propargyloxime (16c).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.25 (s, 3H, CH_3), 2.45 (t, 1H, J = 2.6 Hz, CH), 4.71 (d, 2H, J = 2.6 Hz, CH_2), 6.98 (m, 1H, 4-H), 7.20 (m, 1H, 5-H), 7.45 (m, 1H, 3-H); (Z-isomer) 2.33 (s, 3H, CH_3), 2.45 (t, 1H, J = 2.6 Hz, CH), 4.80 (d, 2H, J = 2.6 Hz, CH_2), 6.98 (m, 1H, 4-H), 7.20 (m, 1H, 5-H), 7.45 (m, 1H, 3-H). MS *m/z*: 179 (42, M^+), 124 (9), 110 (100), 99 (55), 84 (13), 71 (6), 66 (18), 55 (11), 45 (20), 39 (48).

3-Pyridinecarboxaldehyde O-Methyloxime (17a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 3.96 (s, 3H, CH_3), 7.27 (m, 1H, 5-H), 7.92 (m, 1H, 4-H), 8.03 (s, 1H, CH), 8.51 (m, 1H, 6-H), 8.69 (m, 1H, 2-H). MS *m/z*: 136 (100, M^+), 108 (43), 104 (11), 79 (38), 78 (87), 63 (16), 51 (70), 39 (11).

3-Pyridinecarboxaldehyde O-Ethyloxime (17b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.2 Hz, CH_3), 4.22 (q, 2H, J = 7.2 Hz, CH_2), 7.29 (m, 1H, 5-H), 7.91 (m, 1H, 4-H), 8.05 (s, 1H, CH), 8.56 (m, 1H, 6-H), 8.71 (m, 1H, 2-H). MS *m/z*: 135 (47, M^+-Me), 71 (15), 69 (18), 57 (26), 55 (56), 43 (59), 41 (100), 39 (46).

3-Pyridinecarboxaldehyde O-Propargyloxime (17c).- red crystals, M.p. 53-54°. ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.52 (t, 1H, J = 2.6 Hz, CH), 4.76 (d, 2H, J = 2.6 Hz, CH_2), 7.27 (m, 1H, 5-H), 7.92 (m, 1H, 4-H), 8.08 (s, 1H, CH=), 8.56 (m, 1H, 6-H), 8.72 (m, 1H, 2H). MS *m/z*: 160 (35, M^+), 130 (100), 104 (23), 103 (30), 91 (25), 78 (50), 66 (32), 64 (38), 63 (49), 51 (71), 39 (72).

3-Acetylpyridine O-Ethyloxime (18b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.29 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 2.22 (s, 3H, CCH_3), 4.20 (q, 2H, J = 7.0 Hz, $C\underline{H}_2CH_3$), 7.22 (m, 1H, 5-H), 7.91 (m, 1H, 4-H), 8.53 (m, 1H, 6-H), 8.80 (m, 1H, 2-H). MS *m/z*: 164 (82, M^+), 136 (35), 135 (73), 119 (47), 104 (45), 93 (22), 78 (100), 67 (60), 51 (87), 43 (30), 38 (10).

3-Acetylpyridine O-Propargyloxime (18c).- yellow-brown liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.25 (s, 3H, CH_3), 2.45 (t, 1H, J = 2.6 Hz, CH), 4.76 (d, 2H, J = 2.6 Hz, CH_2), 7.22 (m, 1H, 5-H), 7.91 (m, 1H, 4-H), 8.56 (m, 1H, 6-H), 8.82 (m, 1H, 2-H). MS *m/z*: 173 (49, M+-1), 159 (36), 144 (34), 104 (71), 78 (100), 66 (55), 51 (73), 39 (41).

4-Pyridinecarboxaldehyde O-Methyloxime (19a).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 3.98 (s, 3H, CH_3), 7.38 (m, 2H, 3-H and 5-H), 7.93 (s, 1H, CH), 8.56 (m, 2H, 2-H and 6-H). MS *m/z*: 136 (52, M^+), 109 (45), 94 (43), 79 (36), 78 (64), 66 (25), 51 (100), 50 (57), 39 (20).

4-Pyridinecarboxaldehyde O-Ethyloxime (19b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 4.20 (q, 2H, J = 7.0 Hz, $C\underline{H}_2CH_3$), 7.33 (m, 2H, 3-H and 5-H), 7.93 (s, 1H, CH), 8.56 (m, 2H, 2-H and 6-H). MS *m/z*: 150 (74, M^+), 122 (33), 105 (16), 95 (33), 94 (96), 78 (53), 67 (38), 63 (27), 51 (100), 39 (24).

4-Pyridinecarboxaldehyde O-Propargyloxime (19c).- yellow-brown liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.49 (t, 1H, J = 2.6 Hz, CH), 4.76 (d, 2H, J = 2.6 Hz, CH_2), 7.38 (m, 2H, 3-H and 5-H), 8.02 (s, 1H, CH=), 8.56 (m, 2H, 2-H and 6-H). MS *m/z*: 160 (23, M^+), 131 (38), 130 (100), 103 (38), 93 (21), 78 (60), 66 (36), 51 (95), 39 (96).

4-Acetylpyridine O-Ethyloxime (20b).- colorless liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 1.27 (t, 3H, J = 7.0 Hz, $CH_2C\underline{H}_3$), 2.16 (s, 3H, CCH_3), 4.25 (q, 2H, $C\underline{H}_2CH_3$), 7.49 (m, 2H, 3-H and 5-H), 8.56 (m, 2H, 2-H and 6-H). MS *m/z*: 164 (70, M^+), 136 (28), 119 (58), 108 (75), 95 (24), 78 (87), 67 (16), 51 (100), 42 (17).

4-Acetylpyridine O-Propargyloxime (20c).- yellow-brown liquid, ^{1}H NMR ($CDCl_3$): (E-isomer) δ 2.22 (s, 3H, CH_3), 2.49 (t, 1H, J = 2.6 Hz, CH), 4.78 (d, 2H, J = 2.6 Hz, CH_2), 7.47 (m, 2H, 3-H and 5-H), 8.56 (m, 2H, 2-H and 6-H). MS *m/z*: 174 (24, M^+), 173 (35), 145 (38), 143 (45), 131 (12), 117 (30), 104 (39), 92 (27), 78 (87), 66 (35), 51 (100), 39 (73).

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