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O-ALKYLATION OF FURAN AND THIOPHENE KETOXIMES IN CONDITIONS OF INTERPHASE CATALYSIS IN A LIQUID/SOLID SYSTEM

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Alkylation of 2-furanyl- and 2-thienylalkyl ketoximes with alkyl, allyl, and propargyl halides in the two-phase catalytic system sol. $K_2CO_3/C_6H_6/18$-crown-6 at room temperature causes the formation of mixtures of E- and Z-isomers of the corresponding O-ethers with yields of 32-74%. Partial E/Z*-isomerization takes place during the reaction.*

Furan and thiophene oximes and their O-ethers are of interest as biologically active compounds which exhibit antiulcerative [1], antitumor [2], antibacterial, and antifungal activity [3] and are β-blockers [4, 5], and analgesics [6]. Compounds from this series have been tested as pesticides [7], insecticides [8, 9], bactericides [9], herbicides [10], and as plant growth stimulators [11], intermediate products in agrochemistry and pharmacy [12], and herbicidal detoxicants [13]. The antiprotozoal activity of thiophenaldoxime O-ethers was discovered recently [14].

Furan and thiophene aldehyde and ketone O-alkyloximes have usually been prepared by alkylation of the corresponding oximes with alkyl halides (or dialkyl sulfates) in the presence of NaH in dimethylformamide [1], alkali metal hydroxide in dimethyl sulfoxide [15], or sodium methylate in methanol [14]. There are also methods of preparation of these compounds by reactions of the starting ketones with O-alkylhydroxylamines [1, 16] or addition of ketoximes to propargyl ethers in the KOH/DMSO system.

The use of a two-phase catalytic system — 10% aqueous solution of $NaOH/C_6H_6/Bu_4NX$ (X = Br, HSO_4), or Oct_4NBr — significantly simplifies reactions of alkylation of aromatic and heterocyclic aldoximes and ketoximes [17-20]. However, prolonged boiling of the reaction mixtures is frequently required here [19, 20], and formation of nitrons is observed in alkylation of Z-isomers [17].

We conducted alkylation of 2-furyl- and 2-thienylalkyl ketoximes (I-IX) with different alkyl, allyl, and propargyl halides (R^3Y) in the system solid $K_2CO_3/C_6H_6/18$-crown-6 at room temperature. In these very soft conditions, the corresponding O-ethers were separated in most cases as a mixture of *E*- and Z-isomers with yields of 32-74%. Compounds I and IX were obtained as *E*-isomers, and oxime VI was obtained as a pure Z-isomer. The conditions of conducting the reactions, properties of the products obtained, and the ^1H NMR and mass spectra are reported in Tables 1-3.

Starting ketoximes I-IX were obtained by reacting the corresponding ketones with hydroxylamine hydrochloride in the presence of potassium hydroxide in ethanol [21].

The structure of O-ethers X-XXVII obtained was confirmed by the PMR spectra (Table 2). They exhibited two distinctly different groups of resonance signals. Multiplets with chemical shifts and SSCC characteristic of three or two heterocycle protons were observed in the 6.4-7.6 ppm region, and signals of protons from the alkyl groups of substituents R^1, R^2, and R^3 appeared in the 0.9-4.8 ppm region. The oxime group has a deprotecting effect [22], so that the weak-field signals of α-protons from the R^2 substituent were assigned to the *E*-isomer, and the analogous multiplets in the stronger fields were assigned to the Z-isomer. For the same reason, the signals of the 3-H and 4-H ring protons of the furan and thiophene ring were deprotected, on the contrary, in Z-isomers. Since the ratio of *E*- and Z-isomers of the starting ketoximes and the O-ethers obtained was not the same in most cases, partial *E*/Z-isomerization evidently takes place in alkylation of ketoximes. However, Z-isomers of O-ethers XX-XXII were obtained in all cases in alkylation of Z-oxime VI. It should also be noted that the fraction of Z-isomer increases in alkylation of sterically hindered ketoximes.

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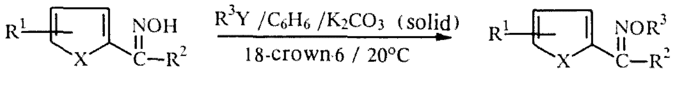
TABLE 1. Conditions of Alkylation of Furyl and Thienyl Ketoximes I-IX and Properties of the O-Ethers X-XXVII Obtained

Oxime	Alkylating agent (R^3Y)	Duration of reaction, h	Product of reaction	Bp, °C/mm Hg	Yield, %
I	$BrCH_2C\equiv CH$	10	X	105...106/10	49
II	C_4H_9Br	9	XI	111...112/10	48
III	CH_3I	7	XII	55...57/10	74
	C_3H_7I	70	XIII	87...90/10	56
IV	C_2H_5Br	7	XIV	103...104/10	63
	C_4H_9Br	29	XV	122...125/10	65
V	$BrCH_2CH_2Cl$	11	XVI	144...147/10	62
	$Br(CH_2)_4Cl$	12	XVII	116...118/1	34
	$CH_2{=}CHCH_2Br$	5	XVIII	117/10	61
	$CH\equiv CCH_2Br$	7	XIX	125...128/10	43
VI	CH_3I	15	XX	90...93/10	32
	C_2H_5I	12	XXI	112...114/10	53
	$CH_2{=}CHCH_2Br$	9	XXII	125...127/10	49
VII	C_2H_5I	4	XXIII	90...91/1,2	69
VIII	CH_3I	13	XXIV	85...87/0,5	37
	C_2H_5I	15	XXV	140/10	47
	$Br(CH_2)_4Cl$	13	XXVI	140...143/1	36
IX	C_2H_5Br	5	XXVII	84...85/1	72



I - IX

X - XXVII

I X = O, R^1 = H, R^2 = Me; II X = O, R^1 = H, R^2 = Et; III X = O, R^1 = H, R^2 = *i*-Pr; IV X = O, R^1 = 5-Me, R^2 = *i*-Pr; V X = S, R^1 = H, R^2 = Me; VI X = S, R^1 = H, R^2 = *i*-Pr; VII X = S, R^1 = H, R^2 = $CHEt_2$; VIII X = S, R^1 = 5-Br, R^2 = Et; IX X = S, R^1 = 3-Br, R^2 = Me; X X = O, R^1 = H, R^2 = Me, R^3 = $CH_2C\equiv CH$; XI X = O, R^1 = H, R^2 = Et, R^3 = Bu; XII X = O, R^1 = H, R^2 = *i*-Pr, R^3 = Me; XIII X = O, R^1 = H, R^2 = *i*-Pr, R^3 = Pr; XIV X = O, R^1 = 5-Me, R^2 = *i*-Pr, R^3 = Et; XV X = O, R^1 = 5-Me, R^2 = *i*-Pr, R^3 = Bu; XVI X = S, R^1 = H, R^2 = Me, R^3 = C_2H_4Cl; XVII X = S, R^1 = H, R^2 = Me, R^3 = C_4H_8Cl; XVIII X = S, R^1 = H, R^2 = Me, R^3 = $CH_2CH{=}CH_2$; XIX X = S, R^1 = H, R^2 = Me, R^3 = $CH_2C\equiv CH$; XX X = S, R^1 = H, R^2 = *i*-Pr, R^3 = Me; XXI X = S, R^1 = H, R^2 = *i*-Pr, R^3 = Et; XXII X = S, R^1 = H, R^2 = *i*-Pr, R^3 = $CH_2CH{=}CH_2$; XXIII X = S, R^1 = H, R^2 = $CHEt_2$, R^3 = Et; XXIV X = S, R^1 = 5-Br, R^2 = Et, R^3 = Me; XXV X = S, R^1 = 5-Br, R^2 = Et, R^3 = Et; XXVI X = S, R^1 = 5-Br, R^2 = Et, R^3 = C_4H_8Cl; XXVII X = S, R^1 = 3-Br, R^2 = Me, R^3 = Et

The interphase catalytic method of alkylation of 2-furyl- and 2-thienylalkyl ketoximes is thus suitable for synthesis of the corresponding O-ethers.

EXPERIMENTAL

The PMR spectra were made on a Bruker WH-90/DS spectrometer in $CDCl_3$ or DMSO-D_6, TMS internal standard. The mass spectra were made on a Kratos MS-25 chromatograph—mass spectrometer with an ionizing electron energy of 70 eV. The GLC analysis was conducted on a Chrom-5 chromatograph with a flame-ionization detector and a glass column packed with 5% OV-17 on Chromosorb W-HP (80-100 mesh); the temperature of the analysis was 160-220°C. The melting point was determined on a Boetius stage and is reported without correction. 2-Acetylfuran, 2-acetylthiophene, 2- and 3-bromothiophenes, and 18-crown-6 were from Fluka.

2-Methyl-1-(2-furyl)-1-propanone and 2-methyl-1-(5-methyl-2-furyl)-1-propanone were prepared by alkylation of 2-acetylfuran and 5-methyl-2-acetylfuran with methyl iodide in conditions of IPC as described in [23]. 2-Methyl-1-(2-thienyl)-1-

TABLE 2. Data from PMR Spectra of *E*- and *Z*-Isomeric O-Ethers of Ketoximes X-XXVII in $CDCl_3$

Compound	Stereoisomer, %	Chemical shifts, ppm, SSCC* (*J*), Hz			
		furan and thiophene ring protons			R² and R³ substituent protons
		3-H	4-H	5-H(CH_3)**	
X	80(*E*)	6,67	6,44	7,47	2,19 (CH_3); 2,48 ($\equiv CH$); 4,80 (CH_2)
	20(*Z*)	7,34	6,52	7,46	2,27 (CH_3); 2,48 ($\equiv CH$); 4,77 (CH_2)
XI	60(*E*)	6,60	6,42	7,47	0,95 ($C_3H_6C\underline{H}_3$); 1,16 ($CH_2C\underline{H}_3$); 1,64 (CH_2CH_2); 2,63 ($C\underline{H}_2CH_3$); 4,20 (OCH_2)
	40(*Z*)	7,30	6,50	7,43	0,95 ($C_3H_6C\underline{H}_3$); 1,21 ($CH_2C\underline{H}_3$); 1,64 (CH_2CH_2); 2,66 ($C\underline{H}_2CH_3$); 4,20 (OCH_2)
XII	30(*E*)	6,62	6,41	7,44	1,26 ($CH\underline{Me}_2$); 3,40 (CH); 3,96 (OCH_3)
	70(*Z*)	7,27	6,49	7,42	1,24 ($CH\underline{Me}_2$); 3,18 (CH); 3,98 (OCH_3)
XIII	30(*E*)	6,60	6,40	7,45	0,97 ($CH_2CH_2C\underline{H}_3$); 1,27 ($CH\underline{Me}_2$); 1,71 ($CH_2C\underline{H}_2CH_3$); 3,44 (CH); 4,12 (OCH_2)
	70(*Z*)	7,33	6,49	7,43	0,99 ($CH_2CH_2C\underline{H}_3$); 1,24 ($CH\underline{Me}_2$); 1,71 ($CH_2C\underline{H}_2CH_3$); 3,18 (CH); 4,14 (OCH_2)
XIV	40(*E*)	6,50	6,00	(2,32)	1,27 ($CH\underline{Me}_2$); 1,29 ($CH_2\underline{CH}_3$); 3,38 (CH); 4,20 (OCH_2)
	60(*Z*)	7,20	6,09	(2,33)	1,24 ($CH\underline{Me}_2$); 1,32 ($CH_2C\underline{H}_3$); 3,17 (CH); 4,20 (OCH_2)
XV	40(*E*)	6,50	5,99	(2,33)	0,95 ($C_3H_6C\underline{H}_3$); 1,27 ($CH\underline{Me}_2$); 1,54 (CH_2CH_2); 3,36 (CH); 4,16 (OCH_2)
	60(*Z*)	7,19	6,09	(2,33)	0,95 ($C_3H_6\underline{CH}_3$); 1,23 ($CH\underline{Me}_2$); 1,54 (CH_2CH_2); 3,16 (CH); 4,16 (OCH_2)
XVI	85(*E*)	7,23	7,01	7,28	2,27 (CH_3); 3,75 (CH_2Cl); 4,36 (OCH_2)
	15(*Z*)	7,47	7,09	7,54	2,33 (CH_3); 3,76 (CH_2Cl); 4,37 (OCH_2)
XVII	70(*E*)	7,21	7,01	7,26	2,23 (CH_3); 1,92 ($CH_2C\underline{H}_2C\underline{H}_2CH_2$); 3,60 ($CH_2Cl$); 4,19 ($OCH_2$)
	30(*Z*)	7,44	7,09	7,53	2,34 (CH_3); 1,92 ($CH_2C\underline{H}_2C\underline{H}_2CH_2$); 3,60 ($CH_2Cl$); 4,19 ($OCH_2$)
XVIII	90(*E*)	7,21	7,00	7,26	2,26 (CH_3); 4,67 (OCH_2); 5,22 и 5,34 ($=CH_2$); 6,04 ($CH=$)
	10(*Z*)	7,46	7,08	7,55	2,34 (CH_3); 4,75 (OCH_2); 5,20 и 5,40 ($=CH_2$); 6,04 ($CH=$)
XIX	85(*E*)	7,22	6,98	7,24	2,27 (CH_3); 2,47 ($\equiv CH$); 4,75 (CH_2)
	15(*Z*)	7,44	7,07	7,50	2,36 (CH_3); 2,47 ($\equiv CH$); 4,80 (CH_2)
XX	100(*Z*)	7,4...7,6	7,07	7,4...7,6	1,28 (CH_3); 3,15 (CH); 4,02 (OCH_2)
XXI	100(*Z*)	7,49	7,08	7,47	1,29 ($CH\underline{Me}_2$); 1,37 ($CH_2C\underline{H}_3$); 3,17 (CH); 4,28 (CH_2CH_3)
XXII	100(*Z*)	7,49	7,09	7,48	1,28 ($CH\underline{Me}_2$); 3,17 ($C\underline{H}Me_2$); 4,74 (OCH_2); 5,22 и 5,37 ($=CH_2$); 6,10 ($CH=$)
XXIII	100(*Z*)	7,49	7,06	7,45	0,90 ($CH(CH_2C\underline{H}_3)_2$); 1,36 ($CH_2C\underline{H}_3$); 1,72 ($CH(C\underline{H}_2CH_3)_2$); 2,75 ($CH$);4,28 ($C\underline{H}_2CH_3$)
XXIV	70(*E*)	6,96	6,93	—	1,14 ($CH_2C\underline{H}_3$); 2,65 (CH_2); 3,93 (OCH_3)
	30(*Z*)	7,16	7,05	—	1,25 ($CH_2C\underline{H}_3$); 2,70 (CH_2); 4,02 (OCH_3)
XXV	35(*E*)	6,93	6,91	—	1,15 ($CH_2C\underline{H}_3$); 1,29 ($OCH_2C\underline{H}_3$); 2,65 ($C\underline{H}_2CH_3$); 4,17 (OCH_2)
	65(*Z*)	7,15	7,04	—	1,25 ($CH_2C\underline{H}_3$); 1,38 ($OCH_2C\underline{H}_3$); 2,68 ($C\underline{H}_2CH_3$); 4,29 (OCH_2)
XXVI	40(*E*)	6,97	6,93	—	1,25 ($CH_2C\underline{H}_3$); 1,94 ($CH_2C\underline{H}_2C\underline{H}_2CH_2$); 2,65 ($C\underline{H}_2CH_3$); 3,61 ($CH_2Cl$); 4,22 ($OCH_2$)
	60(*Z*)	7,16	7,06	—	1,15 ($CH_2C\underline{H}_3$); 1,94 ($CH_2C\underline{H}_2C\underline{H}_2CH_2$); 2,69 ($C\underline{H}_2CH_3$); 3,61 ($CH_2Cl$); 4,22 ($OCH_2$)
XXVII	100(*E*)	—	6,97	7,20	1,36 ($CH_2C\underline{H}_3$); 2,36 (CH_3); 4,23 ($C\underline{H}_2CH_3$)

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*$J_{3,4}$= 3.4, $J_{3,5}$ = 0.8, and $J_{4,5}$ = 1.8 Hz (furan derivatives); $J_{3,4}$ = 3.9, $J_{3,5}$ = 1.2, and $J_{4,5}$ = 5.0 Hz (thiophene derivatives).

**$J_{3,CH3}$ = 0.4 and $J_{4,CH3}$ = 1.0.

TABLE 3. Data from the Mass Spectra of Ketoxime X-XXVII O-Ethers*

Compound	m/z, I_{rel} (%)
X	163 (46, M$^+$), 108(11), 94(100), 83(35), 66(87), 53(16), 39(65), 27(18)
XI	195 (21, M$^+$), 165(13), 150(11), 139(38), 122(62), 107(37), 94(100), 81(26), 57(26), 41(65), 29(98)
XII	167 (53, M$^+$), 152(32), 139(20), 109(30), 94(100), 81(8), 66(7), 59(8), 54(9), 39(32)
XIII	195 (31, M$^+$), 152(31), 138(35), 125(59), 109(22), 94(100), 81(12), 68(11), 55(10), 43(83)
XIV	195 (58, M$^+$), 180(12), 150(17), 139(18), 123(30), 108(100), 97(12), 53(26), 43(61), 27(34)
XV	223 (22, M$^+$), 178(20), 150(41), 136(30), 123(18), 108(100), 82(10), 53(22), 43(59), 29(38)
XVI	203 (56, M$^+$), 141(85), 124(100), 109(39), 97(27), 84(24), 63(15), 57(10), 45(23), 39(62)
XVII	231 (18, M$^+$), 196(100), 141(36), 124(69), 109(30), 99(10), 91(20), 84(50), 55(71), 45(18), 39(60)
XVIII	181 (61, M$^+$), 164(12), 124(29), 110(94), 99(78), 84(15), 78(22), 55(31), 45(20), 39(60), 28(100)
XIX	179 (42, M$^+$), 124(9), 110(100), 99(55), 84(13), 71(6), 66(18), 55(11), 45(20), 39(48)
XX	183 (51, M$^+$), 168(14), 152(32), 137(7), 125(25), 110(100), 97(18), 58(10), 39(31)
XXI	197 (43, M$^+$), 182(10), 152(30), 137(8), 125(19), 110(100), 97(20), 84(9), 58(9), 43(38)
XXII	209 (44, M$^+$), 192(40), 168(17), 137(15), 126(100), 110(77), 97(23), 83(27), 58(14), 41(87)
XXIII	225 (28, M$^+$), 196(34), 180(35), 150(10), 138(12), 125(40), 110(100), 97(22), 55(19), 43(58), 29(57)
XXIV	247 (1, M$^+$), 235(64), 218(41), 188(100), 164(33), 138(45), 110(34), 82(52), 57(22), 45(30), 29(32)
XXV	263 (70, M$^+$), 218(42), 201(19), 188(50), 177(39), 162(19), 136(18), 109(20), 82(44), 45(52), 29(100)
XXVI	325 (21, M$^+$), 290(70), 216(12), 190(33), 160(10), 123(14), 91(40), 55(100), 29(70)
XXVII	249 (68, M$^+$), 204(49), 188(19), 162(23), 140(75), 123(20), 109(40), 82(39), 63(33), 51(100), 39(74)

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*Mass spectra of the *E*- and *Z*-isomers are identical.

propanone and 1-(2-thienyl)-2-ethyl-1-butanone were prepared from 2-acetylthiophene by alkylation with methyl and ethyl iodide, respectively [23]. 1-(5-Bromo-2-thienyl)-1-propanone and 3-bromo-2-acetylthiophene were obtained by Friedel–Crafts acylation of 2-bromo- and 3-bromothiophenes [24].

The results of elemental analysis of the synthesized compounds agreed with the calculated data.

General Method of Preparation of Oximes I-IX. 1-(5-Bromo-2-thienyl)-1-propanone oxime (VIII). Here 9.52 g (136 mmole) of hydroxylamine hydrochloride and 80 ml of 15% KOH solution were added to a solution of 10 g (46 mmole) of 1-(5-bromo-2-thienyl)-1-propanone in 80 ml of ethanol. The mixture obtained was boiled for 12 h (GLC monitoring, 200°C). The precipitated sediment was filtered off and a mixture of (35:65) *E*- and Z-isomers of oxime VIII was obtained, bp = 97-106°C. PMR spectrum, ppm (DMSO-D_6): *E*-isomer: 1.07 (3H, t, CH_3); 2.65 (2H, q, CH_2); 7.18 (1H, s, 3-H); 7.18 (1H, s, 4-H); 11.25 (1H, s, OH); Z-isomer: 1.16 (3H, t, CH_3); 2.68 (2H, q, CH_2); 7.26 (1H, d, 4-H); 7.34 (1H, d, 3-H); 11.88 (1H, s, OH). Mass spectrum, m/z (I_{rel}, %; *E*-, *Z*-): 233 (11, M$^+$), 218 (30), 190 (100), 164 (12), 138 (50), 110 (36), 82 (38), 64 (20), 54 (45), 45 (35), 28 (57). Yield of 7.56 g (71%).

Oximes I-VII and IX were obtained similarly.

***E*-Isomer of 2-acetylfuran Oxime (I) [25].** Prepared from 2-acetylfuran. Reaction time of 10 h, mp = 99-100°C. Published data for *E*-isomer of I: mp = 102-103°C [25]. Yield of 75%.

1-(2-Furyl)-1-propanone Oxime (II), Mixture (60:40) of *E*- and *Z*-Isomers [25]. Obtained from 1-(2-furyl)-1-propanone after 13 h. Yield of 80%.

2-Methyl-1-(2-furyl)-1-propanone Oxime (III), Mixture (20:80) of *E*- and *Z*-Isomers [26]. Obtained from 2-methyl-1-(2-furyl)-1-propanone after 9 h, mp = 25-34°C. Bp = 137-142°C/10 mm Hg. PMR spectrum ($CDCl_3$): *E*-isomer: 1.31 (6H, d, CH_3); 3.59 (1H, septet, CH); 6.24 (1H, d.d, 4-H); 6.72 (1H, d.d, 3-H); 7.48 (1H, d.d, 5-H); 10.0 (1H, br. s, OH);

Z-isomer: 1.27 (6H, d, CH_3); 3.28 (1H, septet, CH); 6.54 (1H, d.d, 4-H); 7.47 (1H, d.d, 3-H); 7.49 (1H, d.d, 5-H); 10.0 (1H, br. s, OH). Mass spectrum, *m/z* (I_{rel}, %; *E*-, *Z*-): 153 (3, M^+), 137 (10), 122 (27), 94 (100), 68 (6), 64 (10), 54 (4), 44 (6), 39 (34), 27 (10). Yield of 52%.

2-Methyl-1-(5-methyl-2-furyl)-1-propanone Oxime (IV), Mixture (45:55) of *E*- and *Z*-Isomers [27]. Obtained from 2-methyl-1-(5-methyl-2-furyl)-1-propanone after 2.5 h, mp = 36-40°C. PMR spectrum ($CDCl_3$): *E*-isomer: 1.31 (6H, d, CH_3), 2.32 (3H, s, CH_3 in furan ring); 3.52 (1H, septet, CH); 6.01 (1H, m, 4-H); 6.52 (1H, m, 3-H); 9.8 (1H, br. s, OH); *Z*-isomer: 1.26 (6H, d, CH_3); 2.34 (3H, s, CH_3 in furan ring); 3.26 (1H, septet, CH); 6.13 (1H, m, 4-H); 7.38 (1H, m, 3-H); 9.8 (1H, br. s, OH). Mass spectrum, *m/z* (I_{rel}, %; *E*-, *Z*-): 167 (25, M^+), 152 (14), 136 (20), 123 (4), 108 (100), 95 (5), 82 (13), 53 (20), 43 (36), 27 (20). Yield of 81%.

2-Acetylthiophene Oxime (V), Mixture (40:60) of *E*- and *Z*-Isomers [4]. Obtained after 10 h. Yield of 82%.

Z-Isomer of 2-methyl-1-(2-thienyl)-1-propanone Oxime (VI) [28]. Obtained from 2-methyl-1-(2-thienyl)-1-propanone after 15 h, mp = 97-99°C. Published data: mp = 99-100°C [28]. PMR spectrum (DMSO-D_6): 1.22 (6H, d, CH_3); 3.22 (1H, septet, CH); 7.14 (1H, dd, 4-H); 7.56 (1H, d.d, 3-H); 7.70 (1H, d.d, 5-H); 11.65 (1H, s, OH). Mass spectrum, *m/z* (I_{rel}, %): 169 (4, M^+), 153 (8), 138 (7), 109 (100), 82 (12), 70 (12), 64 (10), 58 (33), 45 (49), 39 (37), 27 (13). Yield of 73%.

1-(2-Thienyl)-2-ethyl-1-butanone Oxime (VII), Mixture (20:80) of *E*- and *Z*-isomers [29]. Obtained from 1-(2-thienyl)-2-ethyl-1-butanone after 4 h, mp = 79-86°C. Published data: mp = 78-79°C [29]. PMR spectrum (DMSO-D_6): *E*-isomer: 0.81 (6H, t, CH_3); 1.58 (4H, m, CH_2); 2.78 (1H, m, CH); 6.96 (1H, d.d, 4-H); 7.22 (1H, d.d, 3-H); 7.36 (1H, d.d, 5-H); 11.0 (1H, s, OH); *Z*-isomer: 0.81 (6H, t, CH_3), 1.58 (4H, m, CH_2); 2.78 (1H, m, CH); 7.05 (1H, d.d, 4-H); 7.22 (1H, d.d, 3-H); 7.36 (1H, d.d, 5-H); 11.57 (1H, s, OH). Mass spectrum, *m/z* (I_{rel}, %; *E*-, *Z*-): 197 (9, M^+), 180 (15), 168 (13), 153 (20), 110 (100), 78 (75), 70 (22), 55 (43), 45 (38), 39 (60), 29 (28). Yield of 58%.

***E*-Isomer of 3-bromo-2-acetylthiophene Oxime (IX) [4].** Obtained from 3-bromo-2-acetylthiophene after 3 h, mp = 112-116°C. Published data: mp = 111-112°C (for *E*-isomer) [4].

General Method of Alkylation of Oximes I-IX in Conditions of Interphase Catalysis. Alkylation of 1-(5-Bromo-2-thienyl)-1-propanone Oxime VIII with Ethyl Iodide. Here 1.38 g (10 mmole) of powdered K_2CO_3 and 0.81 ml (10 mmole) of ethyl iodide were added to a solution of 1.17 g (5 mmole) of oxime VIII and 0.13 g (0.5 mmole) of 18 crown-6 in 15 ml of benzene. The mixture obtained was stirred at room temperature, monitoring the course of the reaction with GLC, filtered, the excess EtI was distilled from the filtrate at reduced pressure, the residue was vacuum distilled, and compound XXV was obtained, bp = 140°C/10 mm Hg. Yield of 0.61 g (47%).

O-Ethers X-XXIV and XXVI, XXVII were prepared similarly. The properties of compounds X-XXVII are reported in Tables 1-3.

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