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Synthesis of Ethophenprox Analogs

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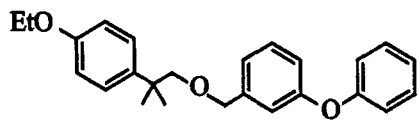
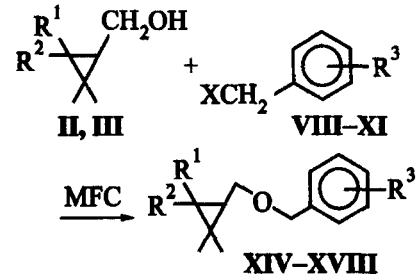
Abstract—The synthesis of ethophenprox analogs was performed by condensation of alcohols with benzyl halides under conditions of the phase transfer catalysis. The ultrasonic irradiation was shown to accelerate the reaction and to increase the yield of ethers. The trends in fragmentation of new generation pyrethroids under the electron impact were established. Insecticidal activity of the compounds obtained was evaluated.

Natural pyrethrins and synthetic pyrethroids are esters of derivatives of cyclopropanecarboxylic acid [1]. It was shown recently that ethers containing structural fragments characteristic of synthetic pyrethroids possessed high insecticidal activity with regards to insects resistant to carbamates and pyrethroids [2]. One thereof designated as ethophenprox (**I**) is widely used in agriculture [3].



I

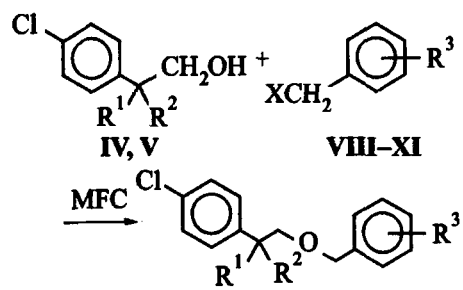
We developed a synthesis of ethophenprox analogs using as synthons acidic and alcoholic components of pyrethroids. Pyrethroids **XIV–XXIX** were prepared by condensation of the appropriate alcohols **II–VII** with benzyl halides **VIII–XIII** under conditions of phase transfer catalysis (PTC) in the system solid phase–liquid, THF, KOH, Bu_4NI, 64°C [4]. The reaction takes from 2 to 25 h, yield of the products 60–89%. We established that ultrasonic irradiation [5] reduced reaction time to 30–60 min and increased



II, III **VIII–XI**

XIV–XVIII

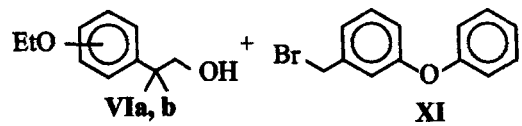
R^1 = $Cl_2C{=}CH$ (**II**, **XIV–XVII**), Me (**III**, **XVIII**); R^2 = H (**II**, **XIV–XVII**), Me (**III**, **XVIII**); X = Br (**VIII**, **X**, **XI**), Cl (**IX**); R^3 = *m*-(*m*-CF_3)C_6H_4O (**VIII**, **XV**), *m*-CF_3 (**IX**, **XVI**), F_5 (**X**, **XVII**), *m*-C_6H_5O (**XI**, **XIV**).



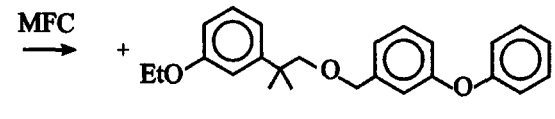
IV, V **VIII–XI**

XIX–XVIII

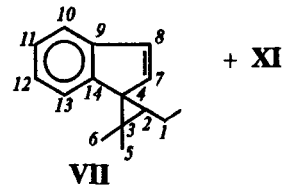
R^1 = *i*-Pr (**IV**, **XIX–XXIII**), Me (**V**, **XXIV–XXVII**); R^2 = H (**IV**, **XIX–XXIII**), Me (**V**, **XXIV–XXVII**); X = Br (**VIII**, **X–XII**), Cl (**IX**, **XIII**); R^3 = *m*-(*m*-CF_3)C_6H_4O (**VIII**, **XX**, **XXV**), *m*-CF_3 (**IX**, **XXI**, **XXVI**), F_5 (**X**, **XXII**), *m*-C_6H_5O (**XI**, **XIX**, **XXIV**), *m*-Br (**XII**, **XXIII**), *m*-, *p*-di-Cl (**XIII**, **XXVII**).



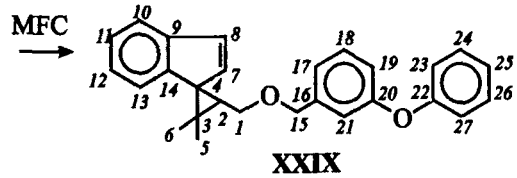
VIa, b **XI**



XVIII



VII



XXIX

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the yield of products to 90–95% (Table 1). The mixture of ethers **I** and **XXVIII** was separated by column chromatography on silica gel (eluent hexane–ethyl ether, 95:5). the spectral characteristics and elemental analysis of products are presented in Tables 2–4.

We established for the mass spectra of new generation pyrethroids the trends in fragmentation under the electron impact (there was no published data on mass spectra of this kind compounds). In the mass spectra of compounds under study (Table 4) were observed molecular ions peaks corresponding to the presumed overall composition. The presence of chlorine atoms in these compounds was confirmed by appearance of ion peaks $M+2^{]+\cdot}$, $M+4^{]+\cdot}$, $M+6^{]+\cdot}$ of relative intensity corresponding to the natural abundance of ^{37}Cl isotope for one (**XIX–XXII**), (**XXIV–XXVI**), two (**XIV–XVII**) and three (**XXVII**) chlorine atoms.

Table 1. Reaction time, yields, refractive indices, IR spectra (ν, cm^{-1}) of ethers

Compd. no.	Name	Time, h[a]	Yield, %[a]	$n_D^{23.2}$	CMe_2	ROR	Other bands[b]
XIV	3,3-Dimethyl-2-(2,2-dichlorovinyl)cyclopropylmethyl *m*-(phenoxy)benzyl ether	3	89	1.5637	1385, 1360, 1170, 1136	1072	3060, 1024 (c); 1584 (C=C)
XV	3,3-Dimethyl-2-(2,2-dichlorovinyl)cyclocyclopropylmethyl *m*-(*m*-trifluoromethylphenoxy)benzyl ether	2 (0.5)	73 (92)	1.5305	1387, 1366, 1178, 1141	1079	3052, 1033 (c); 1595 (C=C); 1334, 1100 (CF_3)
XVI	3,3-Dimethyl-2-(2,2-dichlorovinyl)cyclopropylmethyl *m*-(*m*-trifluoromethyl)benzyl ether	6	89	1.4975	1389, 1374, 1180, 1141	1089	3055, 1035 (c); 1620 (C=C); 1340, 1110 (CF_3)
XVII	3,3-Dimethyl-2-(2,2-dichlorovinyl)cyclopropylmethyl pentafluorobenzyl ether	8	61	1.5471	1378, 1345, 1180, 1144	1080	3050, 1025 (c); 1519 (C=C); 1110 ($C_{ar}F$)
XVIII	2,2,3,3-Tetramethylcyclopropylmethyl *m*-(phenoxy)benzyl ether	3	74	1.5442	1400, 1376, 1160, 1136	1072	3048, 1024 (c); 1033 ($C_{ar}Cl$)
XIX	2-(*p*-Chlorophenyl)-3-methylbutyl *m*-(phenoxy)benzyl ether	8	71	1.5700	1400, 1370, 1180, 1169	1090	1033 ($C_{ar}Cl$)
XX	3-Methyl-2-(*p*-chlorophenyl)butyl *m*-(*m*-trifluoromethylphenoxy)benzyl ether	25 (1)	75 (95)	1.5323	1400, 1370, 1187, 1150	1080	1340, 1110 (CF_3); 1030 ($C_{ar}Cl$)
XXI	3-Methyl-2-(*p*-chlorophenyl)butyl *m*-(trifluoromethyl)benzyl ether	22	68	1.5082	1384, 1360, 1190, 1164	1088	1328, 1124 (CF_3); 1026 ($C_{ar}Cl$)
XXII	3-Methyl-2-(*p*-chlorophenyl)butyl pentafluorobenzyl ether	20	60	1.4955	1400, 1376, 1182, 1140	1079	1110 (CF_3); 1033 ($C_{ar}Cl$)
XXIII	3-Methyl-2-(*p*-chlorophenyl)butyl *m*-bromobenzyl ether	8	72	1.5568	1408, 1384, 1196, 1168	1088	1037 ($C_{ar}Cl$); 672 CBr
XXIV	2-Methyl-2-(*p*-chlorophenyl)propyl *m*-(phenoxy)benzyl ether	12	70	1.5795	1409, 1375, 1175, 1155	1089	1028 ($C_{ar}Cl$)
XXV	2-Methyl-2-(*p*-chlorophenyl)propyl *m*-(*m*-trifluoromethylphenoxy)benzyl ether	18 (0.5)	79 (90)	1.5409	1400, 1360, 1192, 1168	1096	1328, 1128 (CF_3); 1026 ($C_{ar}Cl$)
XXVI	2-Methyl-2-(*p*-chlorophenyl)propyl *m*-(trifluoromethyl)benzyl ether	9	68	1.5440	1384, 1360, 1196, 1168	1072	1328, 1124 (CF_3); 1032 ($C_{ar}Cl$)
XXVII	2-Methyl-2-(*p*-chlorophenyl)propyl *m*-,*p*-dichlorobenzyl ether	17	70	1.5658	1392, 1360, 1184, 1160	1096	1032 ($C_{ar}Cl$)
XXVIII	2-Methyl-2-(*m*-ethoxyphenyl)propyl *m*-(phenoxy)benzyl ether	8	74[c]	1.5695	1392, 1360, 1184, 1160	1096	1248, 1048 ($C_{ar}OEt$)
XXIX	3,3-Dimethylspiro(cyclopropane-1,1'-indene)-2-methyl *m*-(phenoxy)benzyl ether	10	69	1.5537	1395, 1375, 1180, 1140	1080	3060, 1025 (c); 1630 (C=C)

[a] Values in parentheses obtained under ultrasonic irradiation. [b] means cyclopropane. [c] Overall yield of compounds **I** and **XXVIII**.

Table 2. ^{1}H NMR spectra of ethers, δ, ppm ($J_{H,H}$, Hz)

Ether no.	$C\underline{Me}_2$	$Alk\underline{CH}_2$	$\underline{CH}_2Ar$	H arom	Other signals
XIV	1.02 s (*Z*,*syn*),1.04 s (*Z*,*anti*), 1.08 s and 1.17 s (*E*)	3.39m	4.40 s	6.89–7.32	1.26 m $C\underline{H}CH_2$,1.43 m $\underline{H}CC{=}C$, 5.45 s (*Z*) and 5.54 s (*E*)C=CH
XV	1.06 s (*Z*,*syn*),1.13 s (*Zanti*), 1.15 s and 1.17 s (*E*)	3.51 m	4.50 s	7.06–7.44	1.31 m $C\underline{H}CH_2$,1.59 m $\underline{H}CC{=}C$, 5.55 s (*Z*) and5.63 s (*E*)C=CH
XVI	0.99(*Z*,*syn*),1.06 s (*Z*,*anti*), 1.08 s and 1.11 s (*E*)	3.40 m	4.44 s (*Z*) 4.49 s (*E*)	7.30–7.52	1.27 m $C\underline{H}CH_2$,1.47 m $\underline{H}CC{=}C$, 5.41 s (*Z*) and 5.55 s (*E*)C=CH
XVII	0.99(*Z*,*syn*),1.06 s (*Z*,*anti*), 1.12 s and 1.17 s (*E*)	3.54 m	4.60 s (*Z*) 4.68 s (*E*)		1.27 m $C\underline{H}CH_2$,1.69 m $\underline{H}CC{=}C$, 5.55 s (*Z*) and 5.63 s (*E*)C=CH
XVIII	0.95 s (*Z*),1.08 s (*E*)	3.46 d (*J*7.3)	4.45 s	6.87–7.38	0.54 t (*J*7.3)CH
XIX	0.68 d (*J*6.6),0.92 d (*J*6.6)	3.64 d (*J*6.1)	4.36 s	6.91–7.28	1.97 m (*J*7)$\underline{H}CMe_2$,2.53 m $\underline{H}C$-Pr-*i*
XX	0.80 d (*J*6.7),1.05 d (*J*6.7)	3.79 m	4.46 d (*J*12) 4.54 d (*J*12)	7.00–7.05	2.08 m (*J*7)$\underline{H}CMe_2$ 2.66 m (*J*6.7)$\underline{H}C$-Pr-*i*
XXI	0.72 s (*J*6.5),0.97 s (*J*6.5)	3.71 d (*J*6.1)	4.47 s	7.05–7.46	1.99 m (*J*7)$\underline{H}CMe_2$,2.58 m (*J*8) $\underline{H}C$-Pr-*i*
XXII	0.63 d (*J*6.8),0.87 d (*J*6.8)	3.63 d (*J*5.8)	4.43 s	6.97 d (*J*8.5), 7.15 d (*J*8.5)	1.85 m (*J*7.5)$\underline{H}CMe_2$, 2.39 m (*J*7.5)$\underline{H}C$-Pr-*i*
XXIII	0.71 d (*J*6.6),0.95 d (*J*6.6)	3.67 d (*J*5.7)	4.39 s	7.08–7.40	1.99 m (*J*7.5)$\underline{H}CMe_2$,2.59 m (*J*7.5)$\underline{H}C$-Pr-*i*
XXIV	1.29 s	3.40 s	4.41 s	6.91–7.39	
XXV	1.33 s	3.44 s	4.44 s	6.91–7.34	
XXVI	1.26 s	3.44 s	4.50 s	7.24–7.48	
XXVII	1.27 s	3.42 s	4.34 s	7.01–7.45	
XXVIII	1.30 s	3.40 s	4.39 s	6.50–7.35	1.36 t (*J*7)$\underline{Me}CH_2$,3.71 q (*J*7) $C\underline{H}_2Me$
XXIX	1.41 s (*Z*, *syn*),1.43 s (*Z*, *anti*), 1.47 s and 1.49 s (*E*)	3.75 m	4.50 s	6.80–7.25	1.58 m $C\underline{H}CH_2$,6.54 d (*J*6.1) C^7H,6.90 d (*J*6.1)C^8H

Table 3. ^{13}C NMR spectra of ethers, δ, ppm

Compd. no.	$O\underline{C}H_2Ar$	$C\underline{Me}_2$	$C(\underline{C}H_3)_2$	$R\underline{C}H_2O$	$\underline{C}_{ar}Cl$	$\underline{C}_{ar}CF_3$	$\underline{C}_{ar}O$	$\underline{C}_{ar}CH_2O$	$\underline{C}_{ar}Alk$	C arom	Other signals
XIV	*Z*: 27.81 *anti* and 15.80*syn*, *E*: 20.95 and 22.91	*Z*: 22.39, *E*: 23.83	*Z*: 67.11, *E*: 69.78	*Z*: 72.13, *E*: 72.25			156.99 157.38	140.48		117.82, 118.94, 122.20, 123.24, 126.18	$H\underline{C}CH_2$ 28.33 (*Z*) and 29.64 (*E*), $H\underline{C}C{=}C$ 29.90 (*Z*) and 32.96 (*E*), $\underline{C}Cl_2$ 119.07, C=$\underline{C}$H 129.64
XV	*Z*: 27.93 *anti* and 15.89*syn*, *E*: 21.01 and 22.97	*Z*: 22.40, *E*: 23.95	*Z*: 67.49, *E*: 70.10	*Z*: 71.87, *E*: 72.00		132.83		139.07		115.28, 121.54, 126.30, 129.51, 133.03	$H\underline{C}CH_2$ 28.39 (*Z*) and 29.76 (*E*), $H\underline{C}C{=}C$ 30.09 (*Z*) and 33.09 (*E*), $\underline{C}Cl_2$ 118.50, C=$\underline{C}$H 130.29
XVI	*Z*: 27.93 *anti* and 15.86*syn*, *E*: 21.01 and 22.78	*Z*: 22.40, *E*: 23.95	*Z*: 67.49, *E*: 70.10	*Z*: 71.87, *E*: 72.00		132.83		139.07		114.25, 120.55, 125.45, 129.24, 133.35	$H\underline{C}CH_2$ 28.33 (*Z*) and 29.63 (*E*), $H\underline{C}C{=}C$ 30.02 (*Z*) and 32.89 (*E*), $\underline{C}Cl_2$ 119.45, C=$\underline{C}$H 130.16

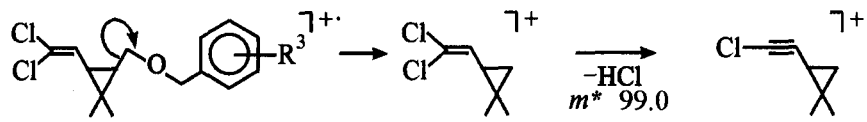
Table 3. (Contd.).

Compd. no.	$O\underline{C}H_2Ar$	$\underline{C}Me_2$	$C(\underline{C}H_3)_2$	$R\underline{C}H_2O$	$\underline{C}_{ar}Cl$	$\underline{C}_{ar}CF_3$	$\underline{C}_{ar}O$	$\underline{C}_{ar}CH_2O$	$\underline{C}_{ar}Alk$	C arom	Other signals
XVII	*Z*: 28.00 *anti* and 15.77 *syn*, *E*: 20.92 and 22.95	*Z*: 22.60, *E*: 24.01	*Z*: 68.12, *E*: 70.67	*Z*: 59.41, *E*: 59.71				110.62		125.94, 135.94, 139.46, 147.45	$H\underline{C}CH_2$ 29.35 (*Z*) and 29.70 (*E*), $H\underline{C}C{=}C$ 29.81 (*Z*) and 32.94 (*E*), $\underline{C}Cl_2$ 121.06, $C{=}\underline{C}H$ 129.29
XVIII	*Z*: 17.05, *E*: 23.67	21.82	63.83	72.08			157.22 157.48	141.11		117.88, 118.03, 119.04, 122.36, 122.48, 123.29	$\underline{C}HCH_2$ 32.56
XIX	20.48 20.97	30.02	72.28	72.55	131.82		157.06 157.34	140.55	141.14	117.57, 117.89, 118.93, 122.02, 123.21, 128.03, 129.65, 129.82, 131.60	
XX	20.52 21.01	30.19	72.42	72.54	131.66	131.81	155.58 158.01	134.53	141.38	115.24, 115.28, 119.64, 119.69, 121.55, 125.63, 128.18, 129.29, 130.03, 130.33	$\underline{C}$-Pr-*i* 52.49
XXI	20.57 21.00	30.13	72.31	72.73	130.95	132.00		139.63	141.21	123.97, 124.03, 124.24, 128.22, 128.77, 129.95	$\underline{C}$-Pr-*i* 52.53
XXII	20.50 20.89	29.77	72.78	54.53	131.99				140.87	128.14, 129.77	$\underline{C}$-Pr-*i* 52.22
XXIII	20.55 21.07	30.08	72.17	72.51	131.90			140.90	141.14	125.83, 128.00, 128.95, 130.07, 130.52, 130.65	$\underline{C}$-Pr-*i* 52.50, CBr 122.51

Table 3. (Contd.).

Compd. no.	$O\underline{C}H_2Ar$	$\underline{C}Me_2$	$C(\underline{C}H_3)_2$	$R\underline{C}H_2O$	$\underline{C}_{ar}Cl$	$\underline{C}_{ar}CF_3$	$\underline{C}_{ar}O$	$\underline{C}_{ar}CH_2O$	$\underline{C}_{ar}Alk$	C arom	Other signals
XXIV	26.15	39.03	72.92	80.01	131.75		157.57 157.20	140.85	141.16	117.62, 117.88, 119.13, 132.05, 123.40, 127.68, 128.17, 129.67, 129.89	
XXV	26.17	39.09	72.79	80.01	130.36	131.78	155.61 159.03	134.64	146.24	115.35, 115.40, 119.30, 119.73, 121.64, 125.64, 127.71, 128.17, 129.18, 132.18	
XXVI	24.98	36.41	71.46	79.20	129.37	131.60		138.90	144.99	122.86, 123.16, 126.54, 127.12, 127.44, 127.70	
XXVII	25.01	38.24	70.70	79.31	131.22 130.61 130.01			139.25	145.89	116.85, 126.40, 127.43, 128.45, 129.77	
XXVIII	25.96	37.00	72.65	80.01			157.12 157.30 160.69	140.91	149.15	110.01, 113.91, 117.59, 118.33, 118.89, 119.02, 121.89, 123.14, 128.82, 129.42, 129.60	$CH_2\underline{C}H_3$ 14.77, $\underline{C}H_2CH_3$ 59.21
XXIX	*Z*:28.98 *anti* and 15.60 *syn*, *E*:20.58 and 20.92	*Z*: 21.71 *E*: 23.01	*Z*: 66.41 *E*: 68.65	*Z*: 71.97 *E*: 72.93			157.54 158.01	140.26	142.73	118.03, 118.10, 119.13, 121.27, 122.02, 123.45, 123.77, 125.46, 128.34, 128.77, 129.55, 130.01	C^2 37.45, C^4 29.62, C^7 135.65, C^8 123.29, C^9 140.46, C^{14} 148.47

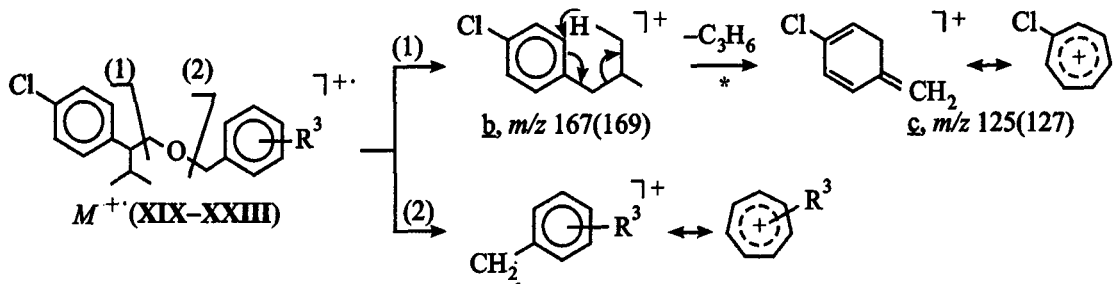
Scheme 1.



$M^{+\cdot}$(**XIV–XVII**) a, *m/z*, 163 (165, 167) a–36, *m/z* 127 (129)

R^3 = *m*-OC_6H_5 (**XIV**), *m*-($OC_6H_4CF_3$-m) (**XV**), *m*-CF_3 (**XVI**), F_5 (**XVII**).

Scheme 2.



$M^{+\cdot}$(**XIX–XXIII**) b, *m/z* 167(169) c, *m/z* 125(127)

d, *m/z* (R^3): 183(*m*-OC_6H_5), 251 [*m*-($OC_6H_4CF_3$-*m*)]. 159(*m*-CF_3), 181 (F_5), 69(*m*-Br).

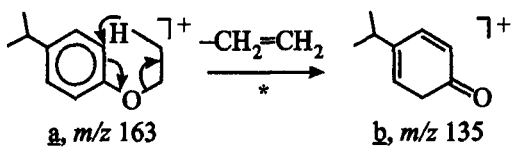
The subsequent decomposition of ions $M^{+\cdot}$ resulted in appearance of relatively weak peaks of fragments that formed by dehalogenation and dehydrohalogenation ions M-Cl^+, M-HCl^+, M-F^+, M-HF^+, M-F_2^+, M-CF_2^+.

The formation of the most abundant (diagnostically significant) ion peaks is due to the cleavage of C–C bonds in β-position with respect to oxygen atom (**XIV–XVIII**) (Scheme 1) and to still greater extent due to cleavage of C–C and C–O bonds in β-position to aromatic systems (benzyl rupture [6]) in all the compounds under consideration (Scheme 2). For compounds **XXIV–XXVII** peaks of ions b and c were registered at *m/z* 153 (155) and *m/z* 125 (127).

The formation of fragments c from b was proved by peaks of metastable ions m^* 102.1 corresponding to transition

$$153^+ \xrightarrow[*]{-C_2H_4} 125^+.$$

The replacement of ethoxy group for chlorine (compounds **I** and **XXVIII**) resulted in appearance of fragments b and c at *m/z* 163 and 135 respectively. The formation of the latter is possible same as in Scheme 2 via rearrangement [7] by loss of ethylene from ethoxy group:



a, *m/z* 163 b, *m/z* 135

In the mass spectra of fluoro-containing compounds **XV–XVII, XX–XXII, XXV, XXVI** analytically significant were the fragments CF_3^+ (*m/z* 69) and for compounds containing trifluoromethyl group **XV, XVI, XX, XXI, XXV, XXVI** appeared ion peaks d-CF_2^+ (*m/z* 109), $C_6H_4CF_3^+$ (*m/z* 145), $C_6H_4F^+$ (*m/z* 95).

The latter apparently formed from fragments *m/z* 145 by the loss of CF_2. This process is characteristic for fragmentation of such compounds [8].

The data on insecticidal activity of 2-methyl-2(*p*-chlorophenyl)propyl (*m*-phenoxy)benzyl ether (**XXIV**) are consistent with the published data: CK_{50} 0.047 at 20°C [9]. At testing of 2-methyl-2(*p*-chlorophenyl)propyl *m*-(*m*-trifluoromethylphenoxy)benzyl ether (**XXV**) we showed that similarly to esters the introduction of a trifluoromethyl group into the phenoxybenzyl moiety decreased the insecticidal activity (CK_{50} 1.5 at 20°C). Equimolar mixture of ethers **I** and **XXVIII** was twice less active (CK_{50} 0.04 at 20°C) than ethophenprox [10] evidencing the lack of insecticidal properties in the *meta*-isomer.

2,2,3,3-Tetramethylcyclopropylmethyl *m*-(phenoxy)benzyl ether (**XVIII**) showed moderate toxicity for flies growing with rising temperature CK_{50} 0.13 at 18°C and 0.03 at 20°C.

EXPERIMENTAL

IR spectra were recorded on spectrometer UR-20 from thin films. ^1H NMR spectra were registered on

Table 4. Elemental analyses and mass spectra of ethers

Ether no.	Found, %				Formula	Calculated, %				Mass spectrum, *m/z* (I_{rel}, %)
	C	H	Cl	F		C	H	Cl	F[a]	
XIV	66.02	5.37	18.93		$C_{21}H_{22}Cl_2O_2$	66.84	5.89	18.79		380 (0.4), 378 (1.4), 376 (1.9) $[M]^+$, 199 (12.0), 183 (100) $[\underline{d}]^+$, 167 (10.0), 165 (41.1), 163 (58.6) $[\underline{a}]^+$, 129 (15.4), 127 (31.4) $[\underline{a}\text{-HCl}]^+$, 93 (d, 8.6), 77 (23.4)
XV	58.97	4.69	15.32	12.62	$C_{22}H_{21}Cl_2F_3O_2$	59.33	4.76	15.92	12.79	448 (0.6), 446 (1.8), 444 (2.7) $[M]^+$, 429 (0.2), 427 (0.3), 425 (0.5) $[M\text{-F}]^+$, 397 (0.1), 395 (0.3), 393 (0.5) $[M\text{-CF}_2\text{H}]^+$, 251 (100) $[\underline{d}]^+$, 167 (3.4), 165 (10.6), 163 (16.7) $[\underline{a}]^+$, 145 (12.0), 129 (5.2), 127 (13.6) $[\underline{a}\text{-HCl}]^+$, 145 (12.0), 107 (22.7), 95 (4.5), 69 (5.2) $[CF_3]^+$
XVI	54.21	4.91	20.65	15.62	$C_{16}H_{17}Cl_2F_3O$	54.40	4.86	20.07	16.14	356 (0.4), 354 (1.1), 352 (1.7) $[M]^+$, 319 (0.8), 317 (2.2) $[M\text{-Cl}]^+$, 190 (59.2), 189 (1.9), 167 (11.2), 165 (40.0), 163 (68.0) $[\underline{a}]^+$, 159 (100) $[\underline{d}]^+$, 145 (73.6), 129 (10.8), 127 (33.6) $[\underline{b}]^+$, 109 (16.4) $[\underline{d}\text{-CF}_2]^+$, 95 (25.2), 91 (66.4), 77 (44.0), 69 (37.2) $[CF_3]^+$, 51 (28.4), 43 (62.4), 39 (37.6)
XVII	48.34	3.64	18.25	25.14	$C_{15}H_{13}Cl_2F_5O$	48.02	3.50	18.90	25.32	378 (0.5), 376 (1.1), 374 (1.8) $[M]^+$, 341 (2.7), 339 (7.6) $[M\text{-Cl}]^+$, 197 (0.4), 195 (2.2), 193 (2.8) $[M\text{-}\underline{d}]^+$, 181 (100) $[\underline{d}]^+$, 167 (8.0), 165 (44.0), 163 (62.4) $[\underline{a}]^+$, 129 (8.8), 127 (32.2) $[\underline{a}\text{-HCl}]^+$, 69 (12.0) $[CF_3]^+$
XVIII	80.88	8.58			$C_{21}H_{26}O_2$	81.24	8.46			310 (2.4) $[M]^+$, 214 (16.8), 183 (17.6) $[\underline{d}]^+$, 127 (3.8), 97 (100) $[\underline{a}]^+$, 55 (21.6)
XIX	75.63	6.98	9.59		$C_{24}H_{25}ClO_2$	75.85	6.63	9.31		382 (7.9), 380 (23.7) $[M]^+$, 337 (3.7) $[M\text{-}i\text{-Pr}]^+$, 214 (5.7), 183 (81.6) $[\underline{d}]^+$, 169 (40.8), 167 (100) $[\underline{a}]^+$, 127 (12.6), 125 (38.2) $[\underline{c}]^+$, 77 (15.8)
XX	67.20	4.46	7.48	12.73	$C_{25}H_{24}ClF_3O_2$	66.89	5.40	7.90	12.69	450 (2.8), 448 (7.8) $[M]^+$, 430 (1.0), 428 (3.4) $[M\text{-HF}]^+$, 251 (100) $[\underline{d}]^+$, 169 (3.2), 167 (7.0) $[\underline{a}]^+$, 145 (1.0), 127 (4.4), 125 (12.2) $[\underline{c}]^+$, 95 (1.2), 69 (1.8) $[CF_3]^+$
XXI	64.36	5.69	10.70	15.22	$C_{19}H_{20}ClF_3O$	63.95	5.66	9.94	15.97	358 (7.2), 356 (20.8) $[M]^+$, 337 (3.4) $[M\text{-F}]^+$, 321 (0.7) $[M\text{-Cl}]^+$, 189 (1.4), 169 (36.0), 167 (100) $[\underline{a}]^+$, 159 (72.0) $[\underline{d}]^+$, 145 (2.9), 127 (20.0), 125 (60.0) $[\underline{c}]^+$, 109 (2.4) $[\underline{d}\text{-CF}_2]^+$, 95 (1.3), 69 (1.0) $[CF_3]^+$

Table 4. (Contd.).

Ether no.	Found, %				Formula	Calculated, %				Mass spectrum, *m/z* (I_{rel}, %)
	C	H	Cl	F		C	H	Cl	F[a]	
XXII	57.70	5.03	8.41	24.42	$C_{18}H_{16}ClF_5O$	57.07	4.27	9.36	25.07	380 (3.0), 378 (8.8) $[M]^+$, 340 (0.8) $[M\text{-}F_2]^+$, 181 (64.0) [d]$^+$, 169 (30.0), 167 (100) [a]$^+$, 127 (23.3), 125 (70.0) [c]$^+$, 69 (2.5) $[CF_3]^+$, 56 (11.7)
XXIII	57.94	4.80	9.16	21.87[a]	$C_{18}H_{20}BrClO$	58.79	5.49	9.64	21.73	
XXIV	75.48	6.26	9.53	-	$C_{23}H_{23}ClO_2$	75.29	6.33	9.66		368 (1.2), 366 (3.6) $[M]^+$, 183 (64.4) [d]$^+$, 155 (32.0), 153 (100) [a]$^+$, 127 (8.0), 125 (19.2) [c]$^+$, 93 (14.4), 77 (20.4)
XXV	65.42	5.29	8.53	13.09	$C_{24}H_{22}ClF_3O_2$	66·28	5.30	8.15	13.10	436 (1.3), 434 (4.0) $[M]^+$, 415 (0.7) $[M\text{-}F]^+$, 251 (33.8) [d]$^+$, 155 (34.0), 153 (100) [a]$^+$, 127 (4.6), 125 (13.0) [c]$^+$
XXVI	63.17	5.36	10.10	16.00	$C_{18}H_{18}ClF_3O$	63.06	5.30	10.34	16.36	344 (0.8), 342 (2.4) $[M]^+$, 323 (0.7) $[M\text{-}F]^+$, 307 (2.3) $[M\text{-}Cl]^+$, 159 (12.0) [d]$^+$, 155 (36.0), 153 (100) [a]$^+$, 145 (7.6), 127 (7.0), 125 (22.0) [c]$^+$, 109 (5.4), 95 (7.2), 69 (9.0) $[CF_3]^+$
XXVII	59.70	4.83	3.62		$C_{17}H_{17}Cl_3O$	59.41	5.00	3.10		346 (0.4), 344 (1.2), 342 (1.3) $[M]^+$, 307 (0.6) $[M\text{-}Cl]^+$, 163 (1.5), 161 (7.9), 159 (14.0) [d]$^+$, 155 (26.6), 153 (100) [a]$^+$, 127 (5.7), 125 (16.6) [c]$^+$
XXVIII	82.74	6.88			$C_{25}H_{28}O_3$	83.08	7.29			376 (10.0) $[M]^+$, 214 (8.3), 200 (22.0), 199 (22.0), 183 (100) [d]$^+$, 163 (88.1) [a]$^+$, 135 (19.0) [c]$^+$, 77 (16.1)
XXIX	84.13	7.23			$C_{27}H_{26}O_2$	84.77	6.87			

[a] For compound **XXIII** Br.

spectrometers Tesla BS-497 (at 100 MHz) and Bruker AM-300 (at 300 MHz). ^{13}C NMR spectra were registered on spectrometers Jeol FX-90Q (22.5 MHz and Bruker AM-300 (75 MHz). Internal reference TMS, solvent $CDCl_3$. Chemical shifts are given in δ scale.

Mass spectra were measured on MX 1303 and MX 1320 instruments at 100–180°C in ionizing chamber and ionizing voltage 70 eV. GLC analyses were carried out on Chrom-5 device , stationary phase 5% SE-30 on carrier N-AW-DMCS, column 1200 mm long, temperature programmed from 50 to 300°C at the rate 14 degmin^{-1}, carrier gas helium. The syntheses with ultrasonic irradiation were performed in the dispergator UZDN-2T with operating frequency 22 kHz.

The insecticidal activity was tested on houseflies by spraying with OML device using ethanol solutions of concn. 0.0001, 0.001, 0.005, 0.01, 0.05, 0.5 and 1.0% with respect to tested compound.

Alkylcyclopropylcarbinols **II, III** [11], and aryl-substituted alcohols **IV** [12, 13], **V** [14] were prepared by reduction with $LiAlH_4$ under standard conditions [15] of methyl ethers of *cis-,trans*-permetrinic, 2,2,3,3-tetramethylcyclopropanecarboxylic, 2-(p-chlorophenyl)isovaleric, and 2-(*p*-chlorophenyl)isobutyric acids. The alkaline hydrolysis under stringent conditions of 2-(p-chlorophenyl)isobutyronitrile afforded 2-(hydroxyphenyl)isobutyric acid as a 1 : 1 mixture of meta and para isomers. Esterification thereof with ethanol provided the corresponding mixture of ethyl (2-ethoxyphenyl)iso-

butyrates that on reduction with $LiAlH_4$ afforded 2-methyl-2(ethoxyphenyl)-1-propanol (**VIa, b**) as equimolar mixture of meta and para isomers. 3,3-Dimethylspiro(cyclopropane-1,1')indene-2-methanol (**VII**) was obtained by reduction of ethyl 3,3-dimethylspiro(cyclopropane-1,1'indene)-2-carboxylate [16] with iBu_2AlH. 3-(m-Trifluoromethyl)phenoxybenzyl bromide (**VIII**) [17, 18] was prepared by bromination of 3-(*m*-trifluoromethyl)phenoxytoluene with NBS in CCl_4 under UV irradiation [19]. *m*-Chloromethylbenzotrifluoride (**IX**) was synthesized by chloromethylation of benzotrifluoride with methyl chloromethyl ether in the presence of $ClSO_3H$ [20]. Pentafluorobenzyl bromide (**X**) was obtained from pentafluorobenzyl alcohol treated with phosphorus tribromide [21, 22].

General procedure of alcohol preparation from esters. To 1.04 g (27.5 mmol) of $LiAlH_4$ in 50 ml of anhydrous ethyl ether at stirring was added 50 mmol of ester in 20 ml of anhydrous ethyl ether. The mixture was stirred under reflux for 4 h. On cooling ice water was added at stirring, then 10% H_2SO_4 (in preparation of compound **III** instead of the acid was added 15% NaOH solution, then water). On separation of the ether layer the water layer was extracted with ether. The combined extracts were washed with NaCl solution and dried with Na_2SO_4.

***cis*-, *trans*-3,3-Dimethyl-2-(2,2-dichlorovinyl)-cyclopropylmethanol (II)** was obtained in 96% yield from ethyl *cis*-, *trans*-permetrinate, n_D^{20} 1.5030. IR spectrum (cm^{-1}): 3336 (O–H); 1612 (C=C); 1390, 1376, 1155, 1135 (CMe_2); 3060, 1020 (cyclopropane). ^1H NMR spectrum (δ, ppm): 1.09 s and 1.13 s (6H, $2CH_3$, *cis*-isomer), 1.18 s (6H, $2CH_3$, *trans*- isomer), 1.31 m (1H, $C\underline{H}CH_2$), 1.59 m (1H, $C\underline{H}CH{=}C$), 2.41 br.s (1H, OH), 3.59 m (2H, $C\underline{H}_2OH$), 5.59 d (1H, $CHC\underline{H}{=}C$, *J* 7.0 Hz, *cis*-isomer), 5.68 d (1H, $CHC\underline{H}{=}C$, *J* 7.0 Hz, *trans*-isomer). Found, %: C 48.80; H 5.85; Cl 35).39. $C_8H_{12}Cl_2O$. Calculated, %: C 49.25; H 5.83; Cl 35.40.

2-Methyl-2(ethoxyphenyl)-1-propanol (VIa, b) was obtained in 88% yield from the equimolar mixture of *ortho*- and *meta*-isomers of ethyl (ethoxyphenyl)isobutyrate. IR spectrum (cm^{-1}): 3400 (O–H); 1392, 1360, 1184, 1155 (CMe_2); 1248, 1052 (C_{ar}–OEt). ^1H NMR spectrum (δ, ppm): 1.28 s (6H, $2CH_3$), 2.39 t (3H, $CH_2C\underline{H}_3$, *J* 8.7 Hz), 2.86 br.s. (1H, OH), 3.52 s (2H, CH_2O), 4.00 q (2H, $C\underline{H}_2CH_3$, *J* 8.7 Hz), 6.77–7.31 m (4H, Ar). Found, %: C 80.84; H 10.12. $C_{12}H_{18}O$. Calculated, %: C 80.84; H 10.20.

***cis, trans*-3,3-Dimethylspiro(cyclopropane-1,1')-indene-2-methanol (VII).** To a solution of 1.55 g (6.4 mmol) of ethyl *cis, trans*-3,3-dimethylspiro-(cyclopropane-1,1'indene)-2-carboxylate in 6.4 ml of heptane under argon at 20°C was added 2.82 ml of 80% solution of $i\text{-}Bu_2AlH$, and the reaction mixture was stirred at this temperature for 1 h. Then the reaction mixture was cooled and treated with 2% HCl solution. The reaction products were extracted into ethyl ether. The ether solution was washed with water and dried with $MgSO_4$. On distilling off the solvent we obtained 1,2 g (94%) of compound **VII** (application of $LiAlH_4$ provided a complicated mixture of products). n_D^{20} 1.5445. IR spectrum (cm^{-1}): 3344 (OH); 1636 (C=C); 1392, 1376, 1184, 1144 (CMe_2); 3064, 1024 (cyclopropane). ^1H NMR spectrum (δ, ppm): 1.13 m (2H, C^2H), 1.34 s (3H, C^5H_3, *cis*-isomer, *syn*-atom), 1.41 s (3H, C^6H_3, *cis*-, *anti*-), 1.43 s (6H, C^5H_3, C^6H_3, *trans*-, *syn*- and *anti*-), 3.90 m (4H, C^1H_2), 4.02 br.s (2H, OH), 6.31 d (1H, C^7H, *cis*-, *J* 5.6 Hz), 6.38 d (1H, C^7H, *trans*-, *J* 5.6 Hz), 6.80 d (1H, C^8H, *cis*-, *J* 5.6 Hz), 6.90 d (1H, C^8H, *trans*-, *J* 5.6 Hz), 7.15–7.42 m (4H, $C^{10}H$–$C^{13}H$). ^{13}C NMR spectrum (δ, ppm): 17.26 C^5 (*cis*-isomer, *syn*-atom); 20.32 C^5 (*trans*-); 21.85 C^6 (*trans*-); 21.99 C^3 (*cis*-); 22.90 C^3 (*trans*-); 27.64 C^6 (*cis*-, *anti*-); 28.08 C^4; 37.91 C^2; 61.12 C^1 (*cis*-); 62.07 C^1 (*trans*-); 121.09, 121.93, 124.04, 128.23, C^{10}–C^{13}; 123.55 C^8; 135.29 C^7; 142.61 C^9; 145.41 C^{14}. Found, %: C 83.99; H 8.10. $C_{14}H_{16}O$. Calculated, %: C 83.95; H 8.07. *m/z*: 200 $[M]^+$, 169 $[M\text{–}CH_2OH]^+$, 142, 141, 129, 116.

General procedure for preparation of ethers. A mixture of 2 mmol of alcohol and 2 mmol of benzyl halide was dissolved in 7 ml of THF, 0.14 g (2 mmol) of 80% KOH and 0.04 g (0.1 mmol) of Bu_4NI was added thereto, and the mixture was stirred at monitoring the process by TLC. The reaction mixture was diluted with ethyl ether and passed through a small layer of silica gel. The solvent was distilled off, and the residue when necessary was separated into components by column chromatography on silica gel.

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