9th International Electronic Conference on Synthetic Organic Chemistry. ECSOC-9
1-30 November 2005. http://www.usc.es/congresos/ecsoc/9/ECSOC9.HTM & http://www.mdpi.net/ecsoc/

[A029]

Synthesis of β-acetylpyrroles from phenacylacetylacetone.

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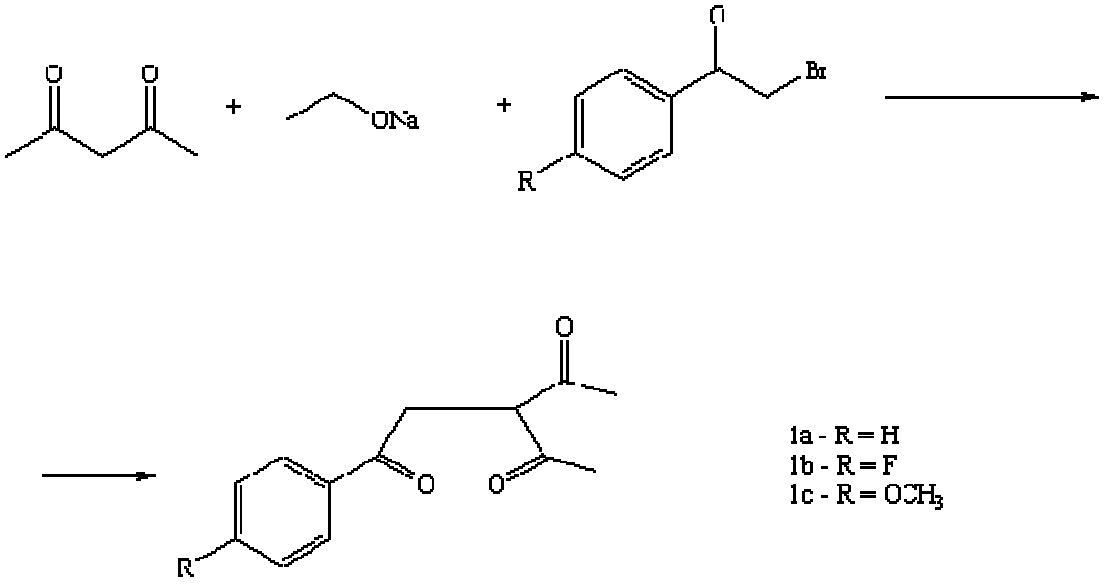
With the purpose of expansion opportunities of pyrroles synthesis method by reaction Paal-Knorr [1] this work is executed.
Earlier we found conditions for effective interaction substitute γ-diketones, containing complicated ethers group, with primary amines, that has allowed to receive the large series new pyrroles with β-substituted ethers or carboxylic group in a β-location after hydrolysis [2,3].
The result of this work is development a method of reception β-acetylpyrroles from phenacylacetylacetones (**1a – 1c**).
As has appeared, phenacylbromides with quantitative yield reacts with Acetylacetone in Alcohol-Ether environment at presence Ethylate sodium (Scheme1.)

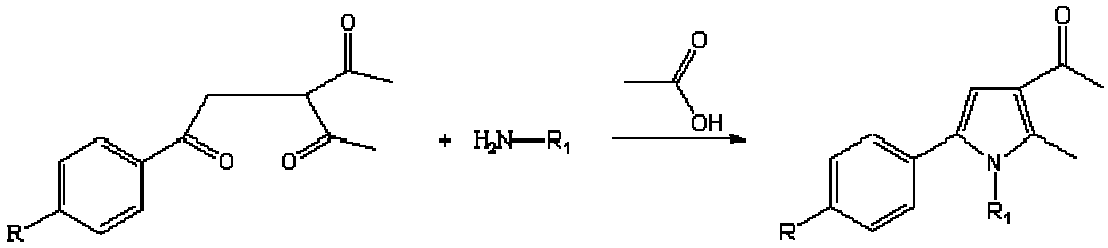
Scheme 1.



1

Products **1a** and **1c** represent at normal temperatures viscous oils. The product **1b** crystallize when it stand. With recrystallization from 50% alcohol (recrystallization yield is 73,5 %) gives temperature of melt 110 – 112°C.
Received γ-diketones (**1a – 1c**) in environment of acetic acid were condensated with a line substitute primary amines.

Scheme 2.



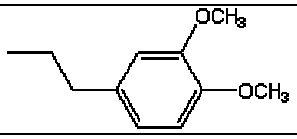
2 (a - q)

The yields and properties synthesized acetylpyrroles (**2a – 2q**) are given in the Table1.

We consider, that the fact of using aliphatic and aromatic amino acids as amines is especially interesting, therefore are formed pyrroles, containing at the same time both of carboxylic and acetylic groups, that make their attractive to use as "building-blocks".

Table 1.

2-methyl-3-acetyl-5-arylpyrroles (2).

№	R	R_1	M.M.	υ, %	Temperature of melt, °C
2a	H	H	199	78,8	177
2в	H	CH_3	213	72,7	92
2c	H	C_6H_5	275	80	94-6
2d	H		363	58	118-9
2e	4-F	H	217	80,5	220
2f	4-F	CH_3	231	78,4	146
2g	4-F	$-CH_2-CH_2-OCH_3$	275	76,4	91

Continue Table 1.

№	R	R_1	M.M.	υ, %*	Temperature of melt, °C
2h	H	$-CH_2-COOH$	257	68,4	194-5
2j	H	$-CH_2-CH_2-COOH$	271	71,3	157
2k	4-F	$-CH_2-COOH$	275	66,2	198-200
2l	4-F	$-CH_2-CH_2-COOH$	289	73,3	170-1
2m	$4-CH_3O$	$-CH_2-COOH$	287	68,7	156-8
2n	$4-CH_3O$	$-CH_2-CH_2-COOH$	301	54,8	170-1
2o	H	$4-C_6H_4-COOH$	319	65,3	209-11
2p	H	$3-C_6H_4-COOH$	319	82	108
2q	4-F	$4-C_6H_4-COOH$	337	65,8	199-200

The yields are given after recrystallization from -iPrOH or EtOH.
Found conditions from realization of this reactions allow successfully scale process and make significant quantities reactives.

References.

1. C. Paal, G. W. Snider. Ber., 1886, 19, 558-560.
2. I. I. Boiko, T. N. Boiko “Synthesis of N-substituted pyrroles from phenacylacetoacetic esters”, 7-th International Electronic Conference on Synthetic Organic Chemistry (ESCOS-7), 2003, [A 027].
3. I. I. Boiko, T. N. Boiko “Synthesis of pyrrolecarboxylic acids from acetonylacetone and acetonylacetic esters”, 8-th International Electronic Conference on Synthetic Organic Chemistry (ESCOS-8), 2004, [A 034].