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# Oxidative carbonylation of dipropargylarylamines at palladium and cupric chlorides catalysis

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## Abstract

The catalytic oxidative methoxycarbonylation reaction of N,N-dipropargylarylamines has been investigated. $PdCl_2$-$CuCl_2$ has been studied as a catalytic system. Consecutive reactions of substitutive and additive methoxycarbonylation have been going in this process, which has been complicated by dimerisation, polymerization and cyclization processes. Apparently the results of process are determined by stability of intermediate reactionary complexes with participation of catalytic system $PdCl_2$-$CuCl_2$. The structures of synthesized cyclic amino triesters are established by analysis of experimental spectra NMR $^1H$ and $^{13}C$, comparison with calculated spectra of possible hypothetic structures and estimation of thermodynamics properties by Joback fragmentation and MOPAC Semi-empirical PM3 methods.

## Introduction

Carbonylation of unsaturated hydrocarbons, alcohols, organic haloids and other substances, catalyzed by salts and complex compounds of VIII group metals – is widely used synthesis method of new carbonyl and alkoxy carbonyl containing compounds [1-6].

The additive carbonylation of alkynyl hydrocarbons at the catalysis of palladium compounds results in the alkenic acids and esters [7], but the substitutive carbonylation of the terminal alkynes leads to esters of alkynic [8-10] or alkylic acids [11]. Key role of formation of intermediated alkynylcopper and alkynylpalladium complexes has been shown in the mechanism of substitutive carbonylation [10].

At the oxidative carbonylation of α,α-tetraalkylsubstituted [12, 13] and unsubstituted [14] dipropargylamines the carboxylic (mono- and di-) derivatives of dimethylenepyrrolidines were obtained. But the cyclopentadienones and more complicated polycyclic compounds were synthesized from the same amines in the presence of Pd(O)-complexes [15, 16]. The carbonylation of propargylamines proceeds efficiently in the presence of catalytic system consisting of tris(dibenzyldenacetone)dipalladium, 1.3-bis(diph- enylphosphino)propane and p-toluenesulfonic acid, affording 2.4-and 2.3-dienamides [17]. α-Methylene-β-lactames are formed directly from the methoxycarbonylation reaction of the benzyl α,α-disubstituted propargylamine under the catalytic action of palladium on carbon in conjuction with potassium iodide, whyle γ-lactams or oxazolines are obtained with unsubstituted or acylated amines [18].

We have shown earlier, that oxidative carbonylation of N-propargylarylamines in the presence of $PdCl_2$ - $CuCl_2$ catalytic system is a convenient way to the new aryl amino acetylenic acids esters [19, 20].

## Experimental

The $^1H$ and $^{13}C$ NMR spectra were obtained on "Mercury-300" spectrometer at 300 MHz. Thin layer chromatography analysis was carried out on "Silufol" silica gel plates. Preparative column chromatography was carried out on silica gel "Silpearl".

*The carbonylation of N,N- dipropargylarylamines (1 a-i )*

The solution of 0.005 mol N,N-dipropargylarylamine ( 1 a-i ) in 30 ml of methanol was added drop by drop on carbon monoxide bubbling and intensive mixing to the solution of 0.0005 mol palladium chloride, 0.02 mol cupric chloride dihydrate and 0.02 mol sodium acetate in

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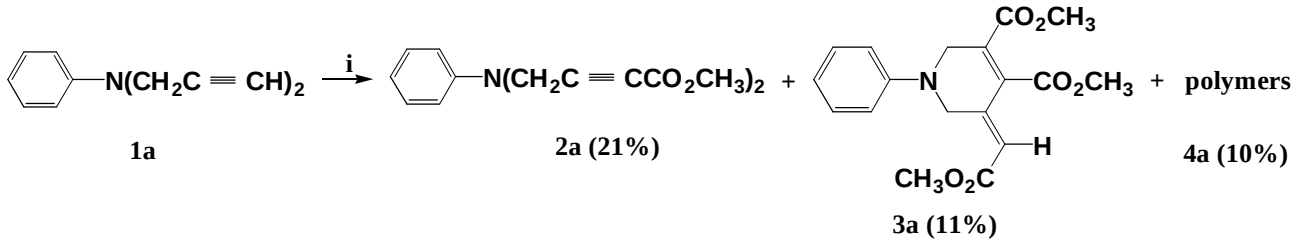
150 ml methanol about 20-40 min. Carbon monoxide was bubbled through reaction mixture until the N,N-dipropargylarylamine ( 1 a-i ) has disappeared, that it has been established by thin layer chromatography method. Reaction mixture was filtered. Methanol was distilled off under reduced pressure. Residue was put on silica gel column and was eluted with benzen: petroleum ether mixture under the increase of it's eluted ability. Chromatographically identical fractions were united. Solvents were distilled off under reduced pressure. Fractions composition was determined by IR and $^1$H NMR spectroscopy methods. Yields of products were determined on the base of theirs $^1$H NMR spectra analysis.

## Results and Discussion

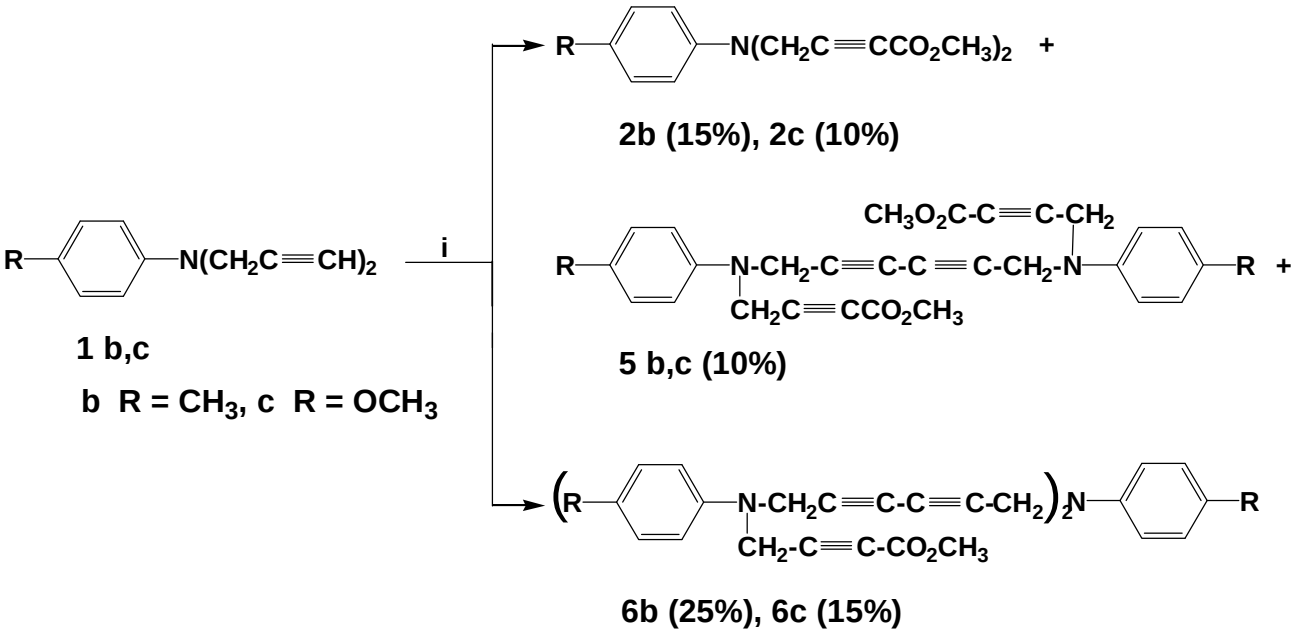
Here we show, that the N,N-dipropargylarylamines (1a-i), obtained by us earlier [20], give products of different types at oxidative carbonylation reaction with palladium chloride and cupric chloride catalysis. The same conditions of the reaction were applied in all cases. The results of the reaction depend on electron nature of substituent and it's position in amines aryl cycles.

The formation of three products has been observed in the case of unsubstituted in cycle N, N-dipropargylaniline (1a) methoxycarbonylation. These products are: amino-diester (2a) in yield up to 21%, cyclic aminotriester (3a) in yield up to 11% and polymers (4a) up to 10%.




i CO, $CH_3OH$, 10% (mol) $PdCl_2$, 4 eq. $CuCl_2$, eq. AcONa per 1 eq. amine (1)

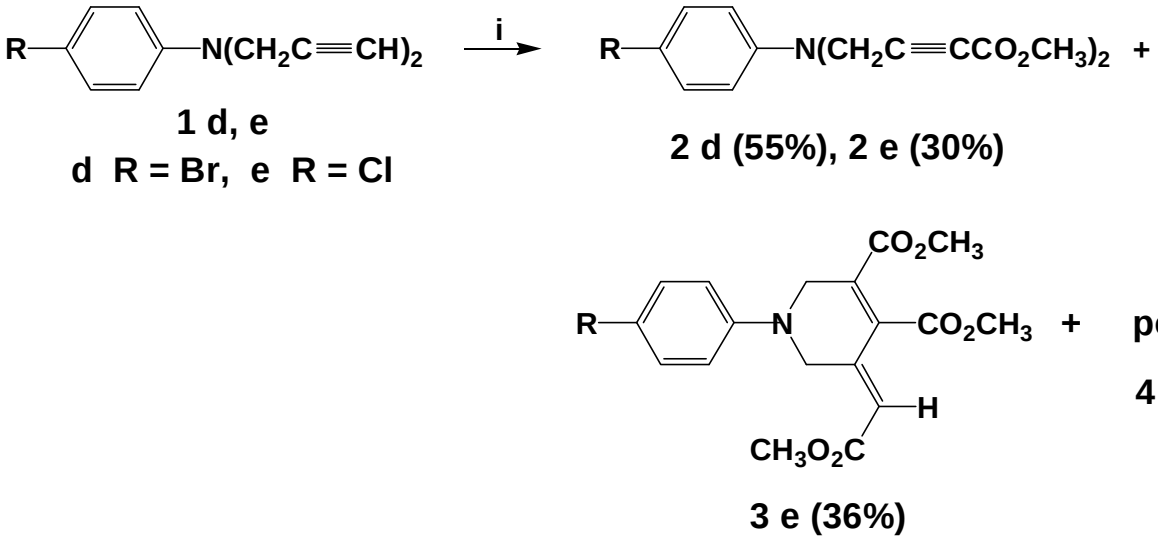
The N,N-dipropargyl p-toluidine (1b) and p-anisidine (1c) behaviours are similar each other.




The formation of monoesters dimers (5 b, c) and trimers (6 b, c) is observed apart from diesters (2 b, c). Polymers have been observed, but not separated from chromatographic silica gel columns.

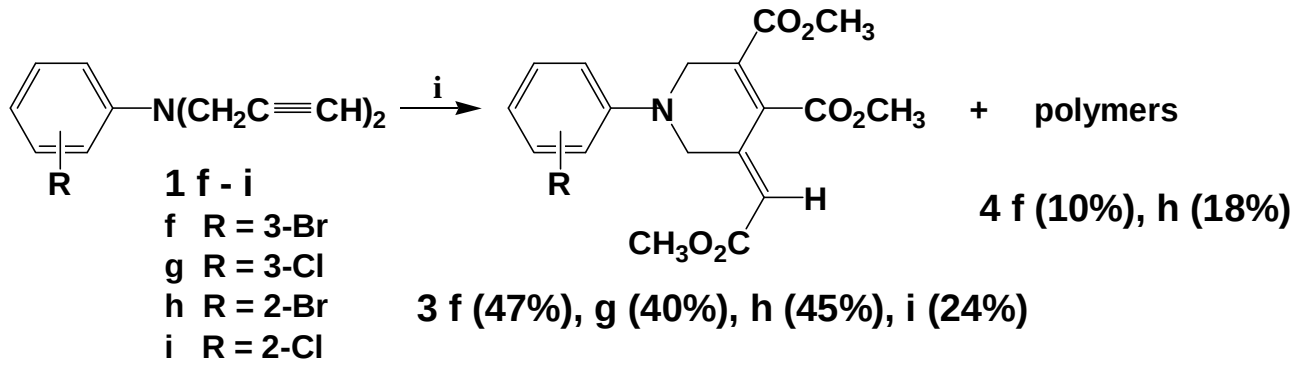
In reactions of the N,N-dipropargylamines, having haloid substituents (1 d-i), the amino diesters (2)

were obtained only for p-substituted (Br, Cl) anilines [21].




The exceptional formation of the aminodiester (2d) was observed for the N,N-dipropargyl p-Br-aniline (1d) methoxycarbonylation. But against the p-Br-aniline (1d) the N,N-dipropargyl p-Cl-aniline (1e) methoxycarbonylation wasn't so singular. There were obtained cyclic triester (2e) in yield from 8 up to 36% and polymer products up to 43% apart from aminodiester (3e) in yield up to 30% in different experiments.

It has been observed the formation only of cyclic triesters (3f-i) in yield 40-47% and polymer products (10-18%) for m- and o-haloid substituted N,N-dipropargylanilines (1f-i) methoxycarbonylation-cases.




It has been demonstated by TLC method for the amine (1e) methoxycarbonylation, that the aminodiester (2e) is formed at the first step of the reaction, then it is converted into cyclo aminotriester (3e) owing to the passing of connected one of amino ester (2e) triple bond additive methoxycarbonilation reaction and cyclization in cyclo aminotriester (3e).

Additive methoxycarbonylation reaction of the aminoester (2e) triple bond may pass on α- or β- C-atom of triple bond, then the cyclization reaction will give the tricarboxylic derivative of methylenepiperideine (3e) or the tricarboxylic derivative of dimethylenepyrrolidine (3'e). See scheme 1.

It is not so easy to choose between these two types of structures by the analysis of experimental NMR ($^1$H or $^{13}$C) spectra of cyclic products (3 e-i) (tables 1, 2). The calculated NMR $^1$H spectra for the tricarboxylic derivatives of methylenepiperideines and dimethylenepyrrolidines structures (3e - 3'e, 3f - 3'f, g - 3'g) are equal in pairs,

**Scheme 1**

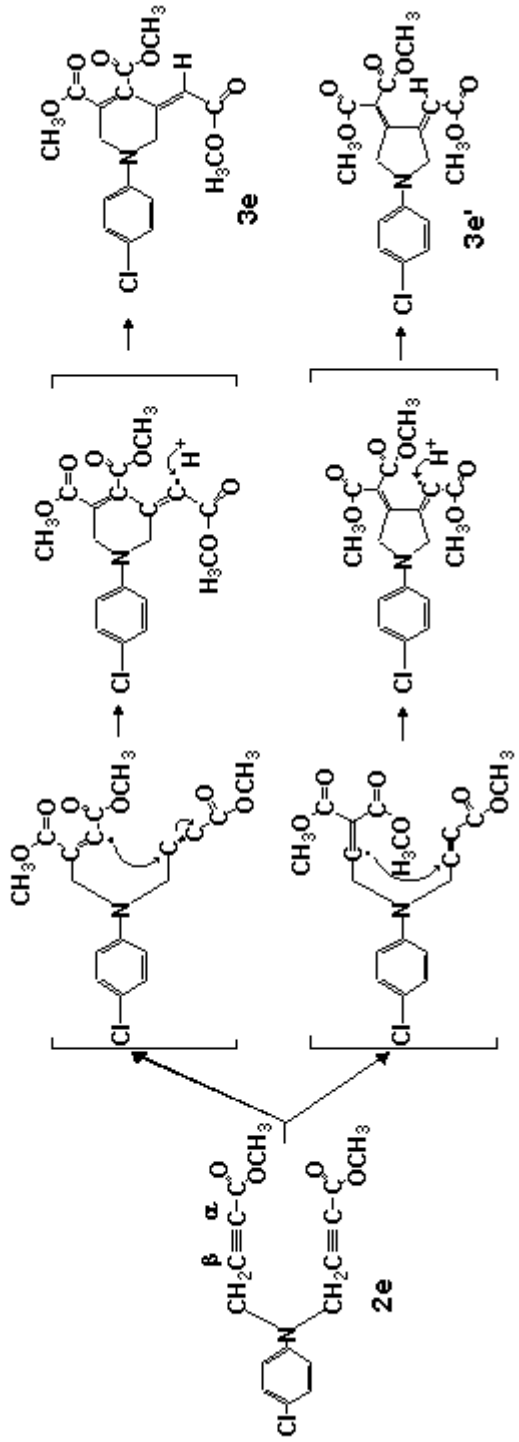
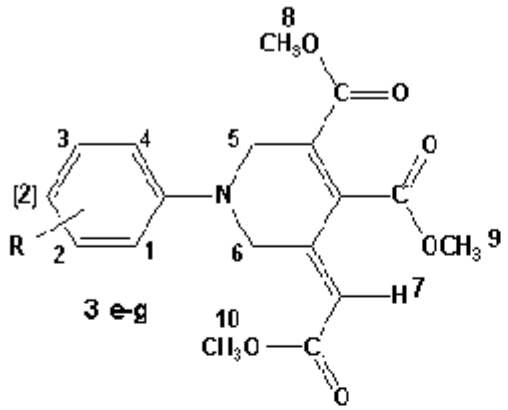
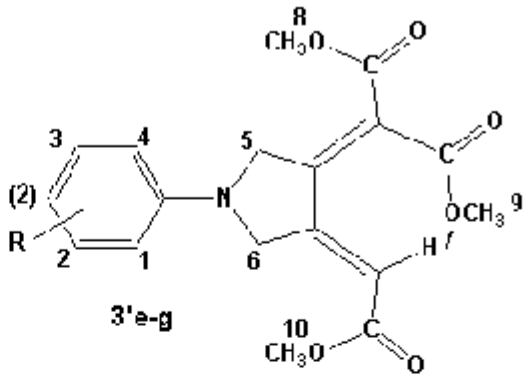


**Table 1**
**NMR $^1H$ spectra of cyclic amino triesters (3 e-g)**




| Compound | R | Spektrum type | H-1 | H-2 | H-3 | H-4 | H-5 | H-6 | H-7 | H-8 | H-9 | H-10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3e** | 4-Cl | e | d 6.60 ($J^3_{HH}$=9.0) | d 7.20 ($J^3_{HH}$=9.0) | d 7.20 ($J^3_{HH}$=9.0) | d 6.60 ($J^3_{HH}$=9.0) | s 4.52 | d 4.51 ($J^4_{HH}$=2.7) | t 6.20 ($J^4_{HH}$=2.6) | s 3.82 | s 3.90 | s 3.76 |
| **3e** | 4-Cl | c | 6.53 | 7.09 | 7.09 | 6.53 | 4.02 | 4.02 | 5.97 | 3.76 | 3.76 | 3.76 |
| **3'e** | 4-Cl | c | 6.53 | 7.09 | 7.09 | 6.53 | 4.02 | 4.02 | 5.97 | 3.76 | 3.76 | 3.76 |
| **3f** | 3-Br | e | t 6.82 ($J^4_{HH}$=2.1) | d 6.87 ($J^3_{HH}$=8.1) | t 7.10 ($J^3_{HH}$=8.1) | dd 6.61 ($J^3_{HH}$=8.1) ($J^4_{III}$=2.1) | s 4.54 | d 4.54 ($J^4_{HH}$=3.9) | t 6.21 ($J^4_{HH}$=2.6) | s 3.83 | s 3.90 | s 3.78 |
| **3f** | 3-Br | c | 6.76 | 6.77 | 6.97 | 6.53 | 4.02 | 4.02 | 5.88 | 3.76 | 3.76 | 3.76 |
| **3'f** | 3-Br | c | 6.76 | 6.77 | 6.97 | 6.53 | 4.02 | 4.02 | 5.88 | 3.76 | 3.76 | 3.76 |
| **3g** | 3-Cl | e | d 6.65 ($J^4_{HH}$=2.1) | d 6.71 ($J^3_{HH}$=7.8) | t 7.18 ($J^3_{HH}$=8.6) | dd 6.54 ($J^3_{HH}$=8.4) ($J^4_{III}$=1.8) | s 4.52 | d 4.51 ($J^4_{HH}$=3.4) | t 6.21 ($J^4_{HH}$=2.6) | s 3.82 | s 3.90 | s 3.77 |
| **3g** | 3-Cl | c | 6.60 | 6.61 | 7.02 | 6.47 | 4.02 | 4.02 | 5.88 | 3.76 | 3.76 | 3.76 |
| **3'g** | 3-Cl | c | 6.60 | 6.61 | 7.02 | 6.47 | 4.02 | 4.02 | 5.97 | 3.76 | 3.76 | 3.76 |

Notes e - experimental in $CDCl_3$, c = 80 mg/ml, δ, p. p.m.; (J, Hz), c - calculated by CS ChemDraw Pro program

**Table 2**

**NMR $^{13}C$ spectra of cyclic amino triesters 3e-g**



**3 e-g**



**3'e-g**

| Compound | R | Spektr. type | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3e | 4-Cl | e | 144.34 | 112.79 | 128.81 | 121.96 | 128.81 | 112.79 | 52.81 | 149.58 | 121.48 |
| 3e | 4-Cl | c | 142.6 | 114.5 | 129.8 | 123.3 | 129.8 | 114.5 | 54.6 | 139.9 | 141.1 |
| 3'e | 4-Cl | c | 142.6 | 114.5 | 129.8 | 123.3 | 129.8 | 114.5 | 58.5 | 158.9 | 122.1 |
| 3f | 3-Br | e | 146.86 | 117.35 | 123.21 | 119.83 | 130.23 | 110.36 | 52.62 | 149.76 | 121.57 |
| 3f | 3-Br | c | 146.7 | 116.4 | 124.0 | 121.3 | 131.6 | 112.1 | 54.6 | 139.9 | 141.1 |
| 3'f | 3-Br | c | 146.7 | 116.4 | 124.0 | 121.3 | 131.6 | 112.1 | 58.5 | 158.9 | 122.1 |
| 3g | 3-Cl | e | 146.73 | 111.61 | 134.91 | 117.34 | 129.94 | 109.94 | 52.65 | 149.36 | 121.57 |
| 3g | 3-Cl | c | 145.9 | 113.5 | 134.7 | 118.4 | 130.8 | 112.2 | 54.6 | 139.9 | 141.1 |
| 3'g | 3-Cl | c | 145.9 | 113.5 | 134.7 | 118.4 | 130.8 | 112.2 | 58.5 | 158.9 | 122.1 |

| Compound | R | Spektr. type | C-10 | C-11 | C-12 | C-13 | C-14 | C-15 | C-16 | C-17 | C-18 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3e | 4-Cl | e | 149.97 | 52.21 | 117.24 | 162.88 | 165.78 | 165.42 | 52.53 | 52.96 | 51.68 |
| 3e | 4-Cl | c | 153.4 | 56.5 | 115.0 | 165.0 | 165.0 | 165.0 | 50.8 | 50.9 | 50.5 |
| 3'e | 4-Cl | c | 153.4 | 59.3 | 115.0 | 165.0 | 165.0 | 165.0 | 50.5 | 50.5 | 50.5 |
| 3f | 3-Br | e | 149.34 | 52.00 | 114.44 | 162.90 | 165.76 | 165.42 | 52.57 | 52.96 | 51.69 |
| 3f | 3-Br | c | 153.4 | 62.5 | 115.0 | 165.0 | 165.0 | 165.0 | 50.8 | 50.9 | 50.5 |
| 3'f | 3-Br | c | 153.4 | 65.3 | 115.0 | 165.0 | 165.0 | 165.0 | 50.5 | 50.5 | 50.5 |
| 3g | 3-Cl | e | 149.74 | 52.08 | 116.9 | 162.88 | 165.75 | 165.41 | 52.53 | 52.94 | 51.68 |
| 3g | 3-Cl | c | 153.4 | 62.5 | 115.0 | 165.0 | 165.0 | 165.0 | 50.8 | 50.9 | 50.5 |
| 3'g | 3-Cl | c | 153.4 | 59.3 | 115.0 | 165.0 | 165.0 | 165.0 | 50.5 | 50.5 | 50.5 |

Notes: e - experimental in $CDCl_3$, c = 80 mg/ml; δ, p. p.m.; c - calculated by CS ChemDraw Pro program

but the NMR $^{13}C$ calculated spectra of the tricarboxylic derivatives of dimethylenepyrrolidine (3'e, 3'f and 3'g) are closer to experimental ones (compare chemical shifts of C-9 atom). Whereas the $^{13}C$ calculated spectra of the methylenepiperideines (3e, 3f and 3g) are closer to experimental ones for others key atoms: C-7 and C-11.

Table 3
Estimation of thermodynamics properties

| R | Compound | Heat of formation kJ/mol [a] | Heat of formation kcal/mol [b] | Gibbs Energy kJ/mol [a] |
|---|---|---|---|---|
| H | 2a | -159.47 | -31.30 | 91.89 |
| | 3a | -870.94 | -176.07 | -506.82 |
| | 3'a | -833.38 | -180.73 | -468.51 |
| 4-Br | 2d | -144.61 | -23.10 | 96.580 |
| | 3d | -856.08 | -168.19 | -502.13 |
| | 3'd | -818.52 | -172.79 | -463.82 |
| 4-Cl | 2e | -186.68 | -37.89 | 70.330 |
| | 3e | -898.15 | -182.66 | -528.38 |
| | 3'e | -860.59 | -187.32 | -490.07 |
| 3-Br | 2f | -144.61 | -23.33 | 92.580 |
| | 3f | -856.08 | -168.12 | -502.13 |
| | 3'f | -818.52 | -172.82 | -463.82 |
| 3-Cl | 2g | -186.68 | -38.02 | 70.330 |
| | 3g | -898.15 | -182.54 | -528.38 |
| | 3'g | -860.59 | -187.26 | -490.07 |

Notes: a by Joback fragmentation method (CS ChemDraw Pro) for T = 298.15K, p = 1 atm.
b by MOPAC Semi-Empirical method PM3. Optimization algorithm Polak-Ribiere.

That is why we have done an attempt to estimate thermodynamics properties of some synthesized and hypothetic structures (see table 3). We can see from this estimation, that the amino diesters (2a, 2e, 2f and 2g) really may be the intermediate compounds in formation of cyclic amino triesters (3a, 3'a, 3e, 3'e, 3f, 3'f and 3g, 3'g). The formation of 6-members cyclic amino triesters (3e, 3f and 3g) is more preferable accordingly Joback fragmentation method. But the formation of 5-members cyclic amino triesters (3'e, 3'f and 3'g) is more preferable according to Semi-empirical method calculations on optimization algorithm Polak-Ribiere.

## Conclusion

The catalytic oxidative methoxycarbonylation reaction of N,N-dipropargylarylamines has been investigated. $PdCl_2$-$CuCl_2$ has been studied as a catalytic system.

It is shown, that consecutive reactions of substitutive and additive methoxycarbonylation have been going in this process, which has been compli-

cated by dimerisation, polymerization and cyclization processes.

The results of process are determined apparently by stability of intermediate reactionary complexes with participation of catalytic system $PdCl_2$-$CuCl_2$, which depend on the electron nature of substituent and it's position in amines aryl cycles.

The structures of synthesized cyclic amino triesters are established by analysis of experimental spectra NMR $^1H$ and $^{13}C$, comparison with calculated spectra of possible hypothetic structures and estimation of thermodynamics properties by Joback fragmentation method.

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