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# ELECTROCHEMICAL SYNTHESIS OF 1,2,3,4,4,5,6-SUBSTITUTED 1,4-DIHYDROPYRIDINES

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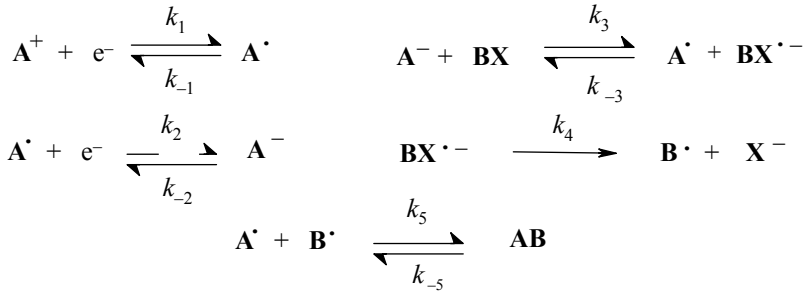
*It has been shown that chemical oxidation of the methyl ester of 3,4,5-trimethoxycarbonyl-1,2,6-trimethyl-1,4-dihydropyridine to the pyridinium salt, requiring forcing experimental conditions, may be replaced by electrochemical oxidation. On electrochemical reduction of 3,4,5-trimethoxycarbonyl-1,2,6-trimethylpyridinium perchlorate in the presence of alkylating agents 1,2,3,4,4,5,6-substituted 1,4-dihydropyridines are obtained.*

**Keywords:** alkyl halides, 1,4-dihydropyridines with completely substituted heterocycle, 4-monosubstituted 1,4-dihydropyridines, pyridinium perchlorate, electrochemical reduction.

Oxidation of dihydropyridines is the basis of their versatile biological activity. It has been established that 3,5-dicyano-1,2,4,4,6-pentamethyl-1,4-dihydropyridine is oxidized in a single one-electron step [1], the reaction product, a stable cation radical, was demonstrated by the EPR spectrum [2].The cation radical for the N-unsubstituted analog is less stable, its EPR spectrum has been recorded successfully only at low temperatures. However, the majority of pharmacologically active compounds based on 1,4-dihydropyridines have at least two protons in the heterocycle (at the C-4 and N-1 atoms). Numerous studies have been devoted to the study of the mechanism of oxidation of dihydropyridines of precisely this type. Proposals for the case in question include transfer of hydride ion [3], a one-electron oxidation with subsequent cleavage of a radical [4], and in the majority of cases a two-electron oxidation with cleavage of two protons [5-7].

Possible cleavage of more stable radicals or cations (in comparison with $H^{\cdot}$ or $H^{+}$) in the process of oxidation may give additional information on the mechanism of action of 1,4-dihydropyridines. It has been shown in the literature that certain anions generated in the process of electrochemical reduction of pyridinium salts (**A**) are electron-donors capable of reducing alkyl halides (**BX**).



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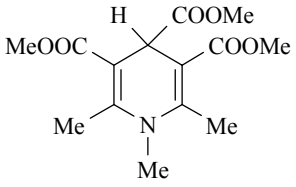
The products of the preparative electroreduction of pyridinium salts in the presence of alkyl halides are alkylated dihydropyridines [8, 9]. The aim of the present work was the synthesis of new dihydropyridines with a completely substituted heterocycle having various substituents in position 4.




**1**

3,4,5-Trimethoxycarbonyl-1,2,6-trimethyl-1,4-dihydropyridine (**1**) was synthesized in a similar manner to the procedure of [10] with subsequent alkylation. [11]. Its structure was confirmed by X-ray structural analysis (Fig. 1).

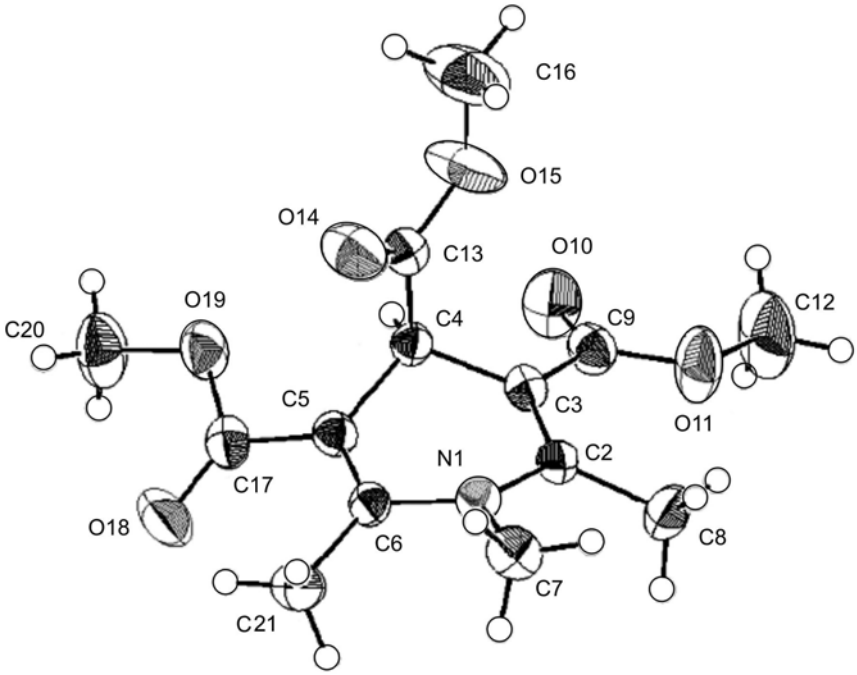
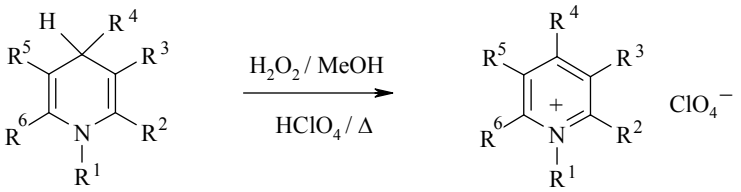



Fig. 1. Steric model of compound 1.

Chemical oxidation of N-substituted 1,4-dihydropyridines occurs only under hard experimental conditions [12, 13].



At the same time 1,4-dihydropyridine **1** in an aprotic medium is oxidized electrochemically in one irreversible step at a potential of +1.14 V (Fig. 2).

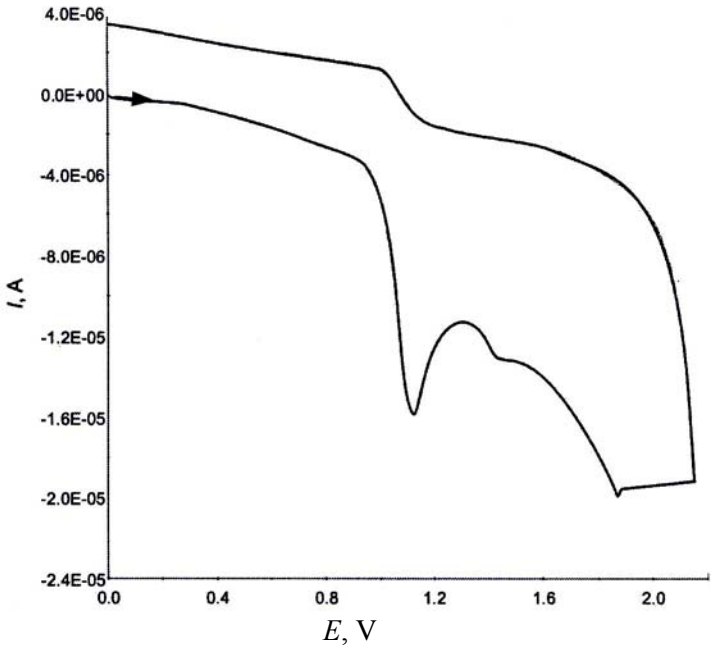
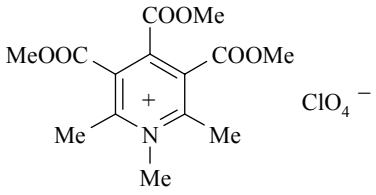



Fig. 2. Electrochemical oxidation of 1,4-dihydropyridine **1** (c = $5\times10^{-4}$ M) at the stationary Pt electrode in 0.1 M $NaClO_4$/MeCN.

On preparative oxidation of dihydropyridine **1** ($E^{ox}$ = +1.20 V) 1 F/mol is consumed. In the $^1$H NMR spectrum ($CDCl_3$), taken of the reaction mixture directly after evaporating the acetonitrile, there were no signals, showing that the products of electrolysis are unsoluable in chloroform. After treatment of the dry residue with water (to remove $NaClO_4$) repeated $^1$H NMR spectrum ($CDCl_3$) correspond to the initial dihydropyridine **1**.

The oxidation product, pyridinium perchlorate **2**, is not soluble in chloroform, its $^1$H NMR spectrum was taken in DMSO-$d_6$ and the structure was confirmed by X-ray structural analysis (Fig. 3).




**2**

The significant difference in solubility of each compound in chloroform was used to separate them on further processing the reaction mixture. The yield of oxidation product, pyridinium perchlorate **2**, did not exceed 50% (Table 1), which corresponds to the average yield on chemical oxidation [13]. Analysis by HPLC of the anolyte untreated after a repeat electrolysis confirms that the electrolyzate contains 50% pyridinium perchlorate **2**. The $^1$H and $^{13}$C NMR spectra, and also the 2D correlation $^1$H–$^1$H-NOESY, $^1$H–$^{13}$C-HSQC, and $^1$H–$^{13}$C-HMBC spectra taken immediately for the untreated anolyte, with saturation of the solvent signal, showed unequivocally that the electrolyzate contains the oxidized form **2** and the protonated dihydropyridine **3**, which is deprotonated in the presence of water regenerating the initial compound **1**.

TABLE 1. Yields of Products of Preparative Oxidation of 1,4-Dihydropyridine **1**

| 1,4-Dihydropyridine **1**, g | Yield, g (mmol) [%] | |
|---|---|---|
| | Pyridinium perchlorate **2** | 1,4-Dihydropyridine **1** |
| 2.01 | 0.97 (2.45) [36.2] | 0.33 (1.10) [16.3] |
| 2.24 | 1.40 (3.55) [47.1] | 0.46 (1.55) [20.6] |
| 2.04 | 1.32 (3.35) [49.5] | 0.40 (1.35) [19.7] |

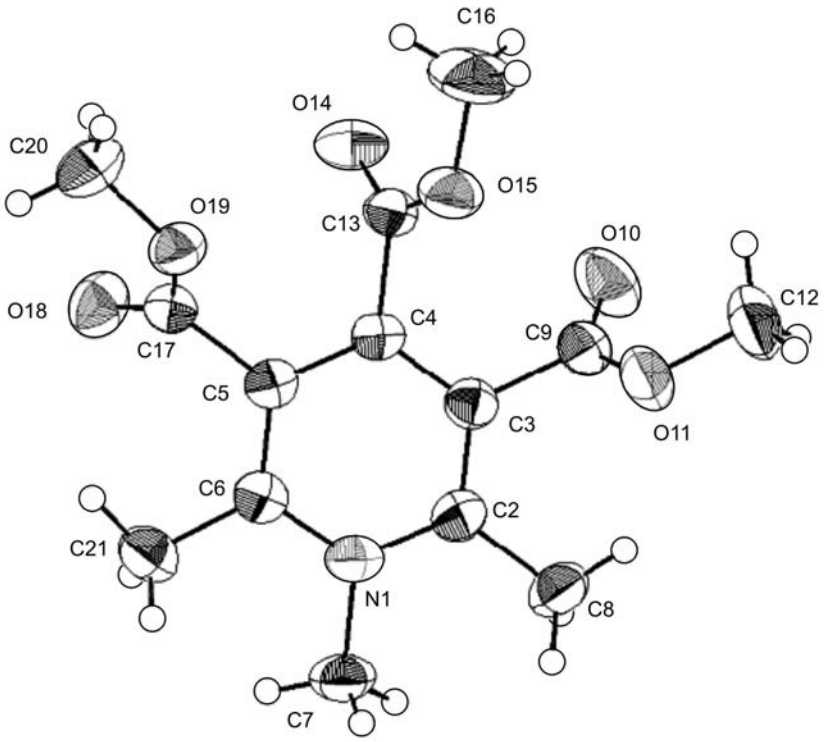
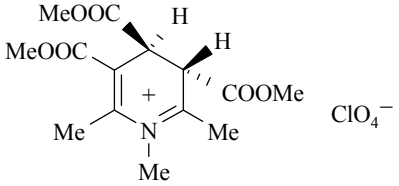



Fig. 3. Steric model of compound **2**.

3,4,5-Trimethoxycarbonyl-1,2,6-trimethylpyridinium perchlorate **2** is reduced in dry DMF in two stages. Transfer of the first electron is effected at -0.67 V, and the second at -1.32 V (Fig. 4). Both steps are quasireversible, the ratio of their cathodic and anodic currents is close to 1, and the difference of potentials of the cathodic and anodic peaks is equal to 69 mV for the first step and 82 mV for the second*. On reducing




**3**

* For the reversible one-electron transfer the ratio of the anodic peak current ($I_a$) to the cathodic ($I_c$) is equal to 1, but the difference in their potentials $E_a - E_c = 0.58$ V.

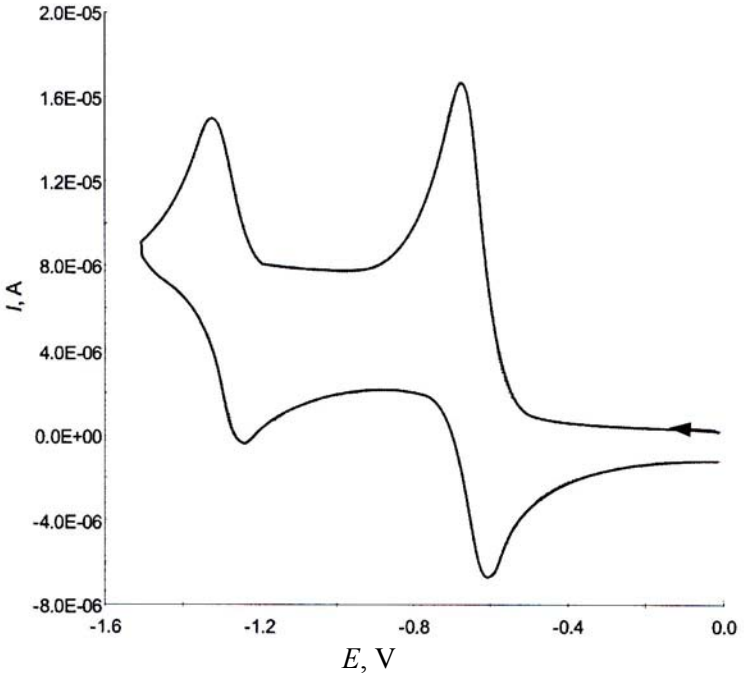



Fig. 4. Electrochemical reduction of pyridinium perchlorate **2** (c = $5\times10^{-4}$ M) at the stationary Pt electrode in 1 M $TBABF_4$/DMF.

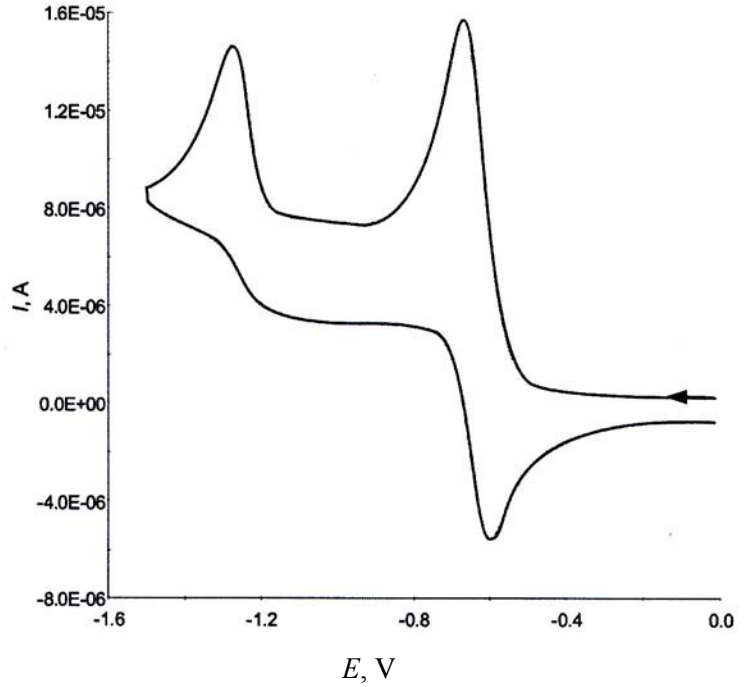
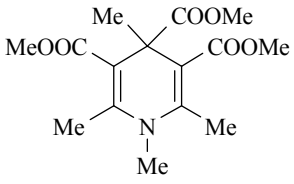
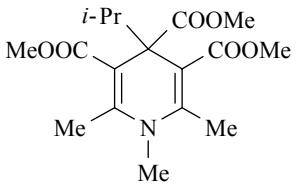



Fig. 5. Electrochemical reduction of pyridinium perchlorate **2** (c = $5\times10^{-4}$ M) in the presence of MeI at the stationary Pt electrode in 0.1 M $TBABF_4$/DMF.

pyridinium perchlorate **2** in the presence of alkyl halides (MeI, EtBr, $Me_2CHBr$) the second reduction step becomes irreversible (Fig. 5). The potential selected for preparative electrolysis $E^{red}$ = -1.50 V is sufficient for the generation of the corresponding anion as a result of transfer of two electrons per molecule of pyridinium perchlorate **2**, but does not provide direct reduction of alkyl halide at the cathode (Table 2). The generated anion is sufficiently strongly electron-donating to be able to reduce the alkyl halide, the potential for reduction of which is displaced by 0.40 V into the cathode region. The obtained anion radical of the alkyl halide is unstable, consequently a rapid and irreversible fission of the halogen–alkyl bond occurs in accordance with the scheme. On carrying out the preparative reduction ($E^{red}$ = -1.50 V) of pyridinium perchlorate **2** in the presence of MeI or *i*–PrBr dihydropyridines **4** and **5** with completely substituted heterocycles are isolated, the structures of which were demonstrated by X-ray structural analysis (Figs. 6 and 7).




**4**




**5**

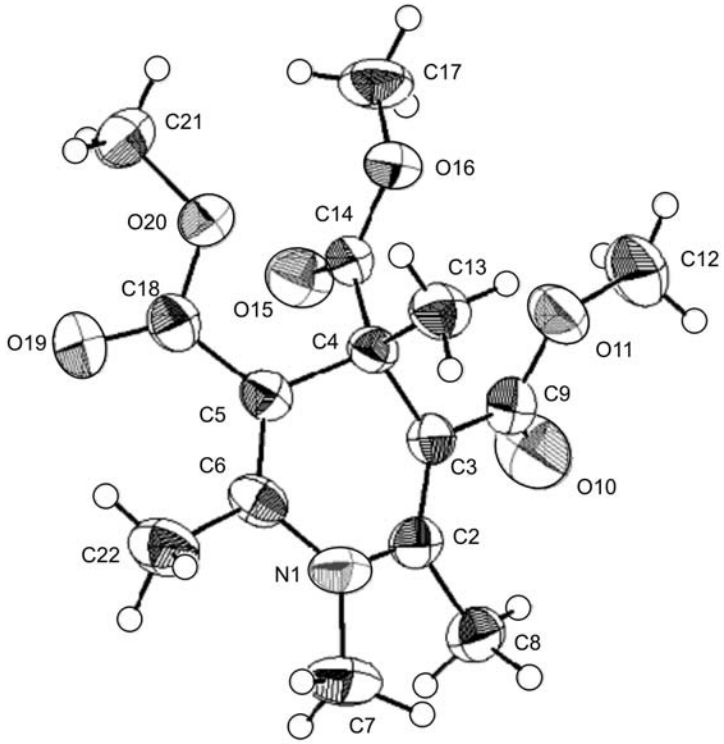



Fig. 6. Steric model of compound **4**.

The deviation from reversibility on reducing pyridinium perchlorate **2** indicates the entry of the generated radical or anion of 1,4-dihydropyridine into secondary chemical reactions, reducing the yield of product. Thus, as a result of protonation of the anion, 1,4-dihydropyridine **1** is isolated in addition to the

TABLE 2. Electrochemical Reduction Potentials of Pyridinium Perchlorate **2** and Alkyl Halides

| | Pyridinium perchlorate 2 | MeI | EtBr | *i*-PrBr |
|---|---|---|---|---|
| $E_1^{red}$, V | -0.67 | -1.70 | -1.70 | -2.00 |
| $E_2^{red}$, V | -1.32 | | | |

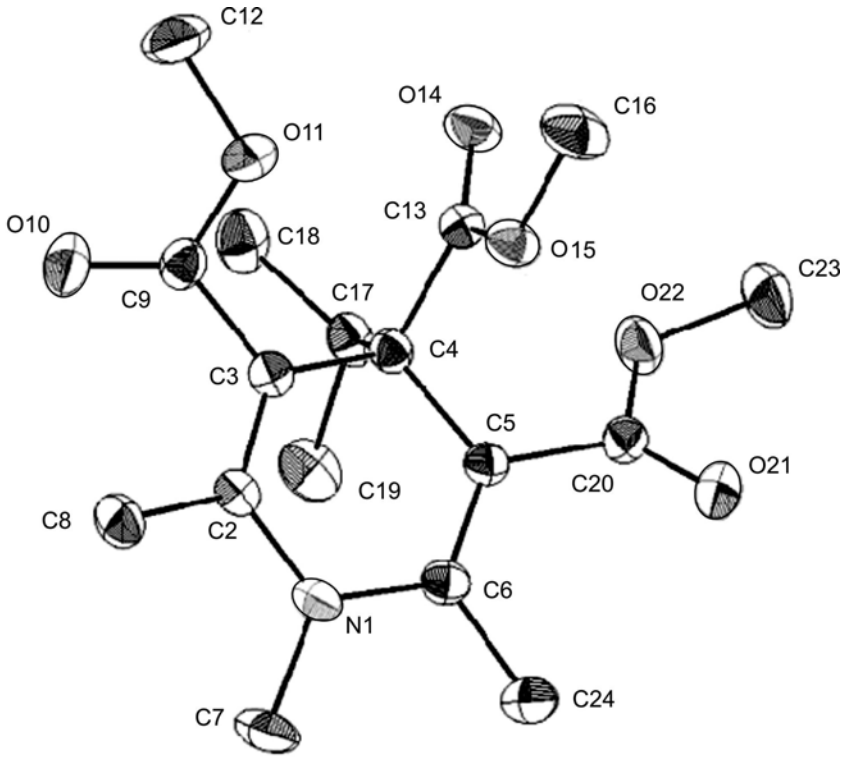
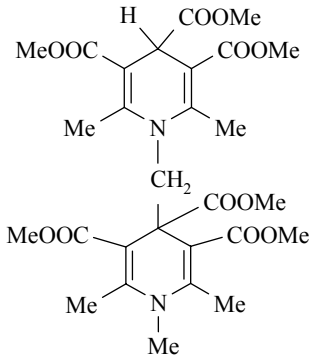



Fig. 7. Steric model of compound **5**.

alkylated dihydropyridines. Compound **6** is also a product of secondary reactions. Its structure was demonstrated by X-ray structural analysis (Fig. 8). The mechanism of formation of compound **6** is being studied.




**6**

TABLE 3. Crystallographic Data for Compounds **1**, **2**, **4-6**

| Characteristic | Compound | | | | |
|---|---|---|---|---|---|
| | **1** | **2** | **4** | **5** | **6** |
| Empirical formula | $C_{14}H_{19}NO_6$ | $C_{14}H_{18}ClNO_{10}$ | $C_{15}H_{21}NO_6$ | $C_{17}H_{25}NO_6$ | $C_{28}H_{36}N_2O_{12}$ |
| $M_r$ | 297.307 | 359.743 | 311.334 | 297.307 | 592.598 |
| Crystal shape | Prisms | Prisms | Needles | Prisms | Plates |
| Monocrystal size, mm | 0.23×0.29×0.42 | 0.07×0.11×0.17 | 0.05×0.08×0.37 | 0.17×0.25×0.39 | 0.11×0.31×0.31 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P\,2_1/a$ | $P\,\bar{1}$ | $P\,\bar{1}$ | $P\,2_1/n$ | $P\,\bar{1}$ |
| Unit cell parameters: | | | | | |
| $a$, Å | 7.9740(3) | 7.7394(2) | 7.4726(3) | 8.9651(2) | 10.5564(3) |
| $b$, Å | 12.5503(5) | 11.3805(3) | 10.1220(5) | 12.1917(4) | 11.1744(3) |
| $c$, Å | 15.1094(8) | 11.7222(3) | 11.4190(7) | 16.7551(6) | 13.9035(5) |
| α, deg | 90 | 116.536(1) | 74.202(2) | 90 | 84.0755(9) |
| β, deg | 102.906(2) | 95.219(1) | 84.726(2) | 99.809(1) | 71.443(1) |
| γ, deg | 90 | 101.587(1) | 74.371(3) | 90 | 68.449(1) |
| $V$, Å$^3$ | 1473.9(1) | 885.34(4) | 800.19(7) | 1804.6(1) | 1445.89(8) |
| Z | 4 | 2 | 2 | 4 | 2 |
| Density, $d$, g/cm$^3$ | 1.340 | 1.485 | 1.292 | 1.249 | 1.361 |
| μ, mm$^{-1}$ | 0.10 | 0.27 | 0.10 | 0.09 | 0.11 |
| Number of independent reflections | 3643 | 3972 | 4226 | 4085 | 6554 |
| observed reflections | 2059 ($I > 3\sigma(I)$) | 3161 ($I > 2\sigma(I)$) | 1700 ($I > 3\sigma(I)$) | 2541 ($I > 2\sigma(I)$) | 4281 ($I > 2\sigma(I)$) |
| parameters refined | 190 | 231 | 199 | 217 | 379 |
| $R$-factor | 0.074 | 0.094 | 0.057 | 0.059 | 0.064 |
| Programs used | SIR [15], maXus [16] | SIR [15], SHELXL [17] | SIR [15], maXus [16] | SIR [15], SHELXL [17] | DETMAX [18], SHELXL [17] |

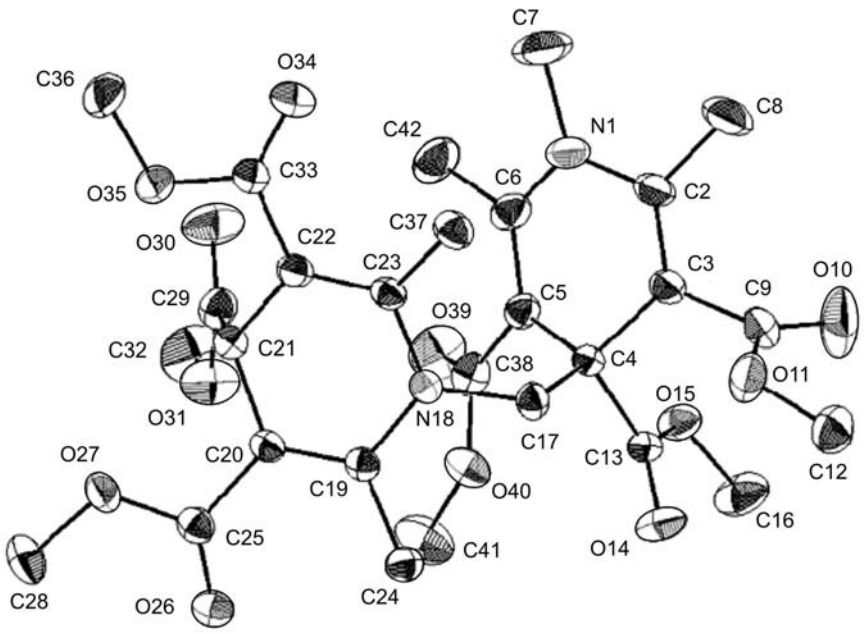
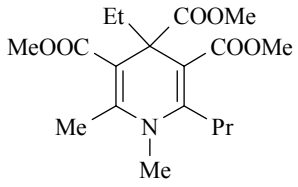



Fig. 8. Steric model of compound **6**.

On reducing pyridinium salt **2** in the presence of EtBr the dihydropyridine **7** is isolated. In it, apart from addition of an ethyl group at position 4 of the ring, one hydrogen atom of the methyl group at position 2 is substituted by an ethyl group.




**7**

Consequently, as a result of the electrochemical reduction of the 3,4,5-trimethoxycarbonyl-1,2,6-trimethylpyridinium salt **2** in the presence of alkylating agents, 1,2,3,4,4,5,6-substituted 1,4-dihydropyridines are obtained, which have not been successfully obtained by classical organic synthesis up to the present time.

## EXPERIMENTAL

Cyclic voltamperograms were taken on a PARSTAT 2273 electrochemical system. Oxidation and reduction potentials were determined at the stationary Pt electrode ($d$ = 2 mm). All potentials were measured relative to a saturated calomel electrode provided with a salt bridge. A Pt wire served as the auxiliary electrode.

Preparative electrolysis (oxidation of dihydropyridine **1** and reduction of pyridinium salt **2**) was carried out using a PAR 170 electrochemical system. Oxidation of dihydropyridine **1** was carried out in an H-shaped cell at a potential of +1.20 V in acetonitrile prepared according to the procedure of [14]. Anhydrous $NaClO_4$, dried in vacuum at 40°C, was used as base electrolyte. The cell was filled with 0.1 M base electrolyte solution (100 ml), compound **1** (2.00 g, 6.7 mmol) was put into the anodic space, platinum meshes (3.5×2.5 cm) served as the anode and cathode, argon was blown through the anode compartment throughout the electrolysis. After the end of electrolysis the reaction mixture was evaporated. To remove $NaClO_4$ the residue was washed with water (5 ml), filtered, and dried. The dry residue was treated with chloroform and filtered. Pyridinium perchlorate **2**, insoluble in chloroform, was obtained. The filtrate contained dihydropyridine **1** (Table 1).

Electrochemical reduction of pyridinium perchlorate **2** was carried out in 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) solution in DMF at a potential of -1.50 V in a stream of argon. Pyridinium perchlorate **2** (1.00 g, 6.5 mmol) was placed in the cathode compartment and alkyl halide (MeI, EtBr, *i*-PrBr) (10 ml) was added. A stirred mercury pool served as the cathode and a graphite rod was the anode. After the end of electrolysis the catholyte was treated with water and extracted with diethyl ether. The reaction mixture obtained was subjected to column chromatography, eluent was petroleum ether–acetone, 2 : 1.

The $^1H$ NMR spectra were recorded on a Varian Mercury 200 (200 MHz) spectrometer, internal standard was HMDS, and were processed with the aid of the NUTS program. The $^1H$ and $^{13}C$ spectra of compound **3** and also the two-dimensional $^1H$–$^1H$-NOESY, $^1H$–$^{13}C$-HSQC, and $^1H$–$^{13}C$-HMBC spectra were recorded on a Varian-Inova (600 MHz) spectrometer fitted with a cryomonitor, in acetonitrile solution at 25°C with the capability for impulse gradient technology. The duration of mixing time for 2D-NOESY was 1 s. The $^1H$–$^{13}C$-HMBC spectra were recorded with an interaction evolution time for the generation of distant correlations of 62.5 ms. A data matrix of size 4098×1024 was used to record all the two-dimensional spectra, which provided $\tau_{2max}$ = 250 ms for $^1H$ on recording along the F2 axis and $\tau_{1max}$ = 100 ms for $^{13}C$ on recording along the F2 axis. To optimize the signal-to-noise ratio the data matrix before Fourier transformation was supplemented with zeros twice and multiplied by the cosine function. Chemical shifts of carbon and hydrogen atoms are given relative to the residual signals of the solvent (2.01 and 116.53 ppm respectively).

For X-ray structural analysis the diffraction pattern for monocrystals of compounds **1**, **2**, and **4-6** were taken at room temperature on a Nonius KappaCCD automatic diffractometer up to $2\theta_{max}$ = 55° ($\lambda_{Mo}$ = 0.71073 Å). The main crystallographic characteristics of compounds **1**, **2**, and **4-6** and also the parameters of the refinement of the crystal structures are given in Table 3.

Elemental analysis was carried out on an EA 1106 automatic analyzer. Melting points were determined on a Boetius instrument. Analysis by HPLC with spectrophotometric detection was carried out on a 655A-11 Liquid Chromatograph, column was Alltima C18 (4.6×250 mm), mobile phase MeCN–0.1% $H_3PO_4$ solution in water. Linear gradient (20 min) from 5 to 95% MeCN. Consumption of mobile phase 0.8 ml/min, wavelength 300 nm. Acros silica gel (0.060-0.200 mm) was used for preparative column chromatography (column 3.5×29 cm), eluent was chloroform–hexane–acetone, 9 : 7 : 1. A check on the progress of reactions and the purity of the compounds obtained was carried out by TLC on Merck silica gel 60 $F_{254}$ plates in the system chloroform–hexane–acetone, 9 : 7 : 1.

**3,4,5-Trimethoxycarbonyl-1,2,6-trimethyl-1,4-dihydropyridine (1)** was synthesized by the procedure of [10]. Yield was 55%, yellow crystals, mp 132-133°C. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 2.46 (6H, s, $CH_3$); 3.16 (3H, s, $NCH_3$); 3.58 (3H, s, $COOCH_3$); 3.73 (6H, s, $COOCH_3$); 4.94 (1H, s, CH). Found, %: C 56.86; H 6.49; N 4.60. $C_{14}H_{19}NO_6$. Calculated, %: C 56.56; H 6.44; N 4.71.

**3,4,5-Trimethoxycarbonyl-1,2,6-trimethylpyridinium Perchlorate (2).** Yield was 49%, white crystalline substance mp 219-220°C. $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 2.84 (6H, s, $CH_3$); 3.93 (9H, s, $COOCH_3$); 4.13 (3H, s, $N^+CH_3$). Found, %: C 42.32; H 4.44; N 3.60. $C_{14}H_{19}NO_6$. Calculated, %: C 42.49; H 4.58; N 3.54.

**3,4,5-Trimethoxycarbonyl-1,2,6-trimethyl-3,4-dihydropyridinium Perchlorate (3).** $^1$H NMR spectrum ($CH_3CN$), δ, ppm: 2.43 (3H, s, $CH_3$); 2.88 (3H, s, $CH_3$); 3,70 (3H, s, $COOCH_3$); 3.71 (3H, s, $COOCH_3$); 3.74 (3H, s, $N^+CH_3$); 3.88 (3H, s, $COOCH_3$); 4.59 (1H, s, $J$ = 0, CH); 4.77 (1H, s, $J$ = 0, CH). $^{13}$C NMR spectrum ($CH_3CN$), δ, ppm: 17.0 (6-$CH_3$); 27.0 (2-$CH_3$); 39.1 (4-C); 41.6 (1-$CH_3$); 50.0 (3-C); 53.9 (5-COO$\underline{C}H_3$); 54.0 (4-COO$\underline{C}H_3$); 55.0 (3-COO$\underline{C}H_3$); 122.3 (5-C); 145.3 (6-C); 165.2 (3,5-$\underline{C}OOCH_3$); 168.9 (4-$\underline{C}OOCH_3$); 188.8 (2-C).

**3,4,5-Trimethoxycarbonyl-1,2,4,6-tetramethyl-1,4-dihydropyridine (4).** Yield 30%, yellow crystalline substance, mp 122-126°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 (3H, s, $CH_3$); 2.25 (6H, s, $CH_3$); 3.16 (3H, s, $NCH_3$); 3.64 (9H, s, $COOCH_3$).

**4-Isopropyl-3,4,5-trimethoxycarbonyl-1,2,6-trimethyl-1,4-dihydropyridine (5).** Yield 32%, yellow crystalline substance, mp 122-123°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm ($J$, Hz): 0.87 [6H, d, $J$ = 7.0, $CH(C\underline{H}_3)_2$]; 2.26 (6H, s, $CH_3$); 2.38 [1H, septet, $J$ = 7.0, $C\underline{H}(CH_3)_2$]; 3.09 (3H, s, $NCH_3$); 3.64 (9H, s, $COOCH_3$).

**3,4,5-Trimethoxycarbonyl-4-(3,4,5-trimethoxycarbonyl-2,6-dimethyl-1,4-dihydro- pyridin-1-ylmethyl)-1,2,6-trimethyl-1,4-dihydropyridine (6).** Yield 20%, yellow crystalline substance. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.56 (6H, s, $CH_3$); 2.59 (6H, s, $CH_3$); 3.59 (6H, s, $COOCH_3$); 3.61 (3H, s, $NCH_3$); 3.68 (2H. s, $NCH_2$); 3,78 (6H, s, $COOCH_3$); 3.81 (6H, s, $COOCH_3$); 4.90 (1H, s, CH).

**4-Ethyl-3,4,5-trimethoxycarbonyl-1,6-dimethyl-2-propyl-1,4-dihydropyridine (7).** Yield 20%, yellow substance, mp 123-125°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm ($J$, Hz): 0.79 (3H, t, $J$ = 7.0, $CH_2C\underline{H}_3$); 0.98 (3H, t, $J$ = 7.0, $CH_2CH_2C\underline{H}_3$); 1.55 (2H, septet, $J$ = 7.0, $CH_2C\underline{H}_2CH_3$); 1.81 (2H, septet, $J$ = 7.0, $C\underline{H}_2CH_3$); 2.23 (3H, s, $CH_3$); 2.45 (1H, m, $J$ = 7.0, $C\underline{H}_2CH_2CH_3$); 2.68 (1H, m, $J$ = 7.0, $C\underline{H}_2CH_2CH_3$); 3.09 (3H, s, $NCH_3$); 3.62 (3H, s, $COOCH_3$); 3.63 (3H, s, $COOCH_3$); 3.65 (3H, s, $COOCH_3$).

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