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OXIRANES IN THE RITTER REACTION. SYNTHESIS OF 6,7- AND 5,8-DIMETHOXY-3,3-DIALKYL-3,4-DIHYDROISOQUINOLINES BY A TANDEM ALKYLATION–CYCLIZATION REACTION

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The interaction of 1,2- or 1,4-dimethoxybenzene with isobutylene oxide and nitriles RCN leads to 1-R-6,7- or 1-R-5,8-dimethoxy-3,3-dimethyl-3,4-dihydroisoquinolines. In the case of 1,2-dimethoxybenzene and cyclohexene oxide the similar reaction is accompanied by rearrangement and 1-R-3,3-tetramethylene-3,4-dihydroisoquinolines are formed in low yield. On using cyanoacetic acid ester and any oxide derivatives of tetrahydroisoquinolylideneacetic acid are formed.

Keywords: veratrole, 1,4-dimethoxybenzene, isoquinoline, nitriles, oxiranes, alkylation, quantum chemical calculations, AM1 method, Ritter reaction, cyclization.

The alkylation of aromatic compounds by olefins [1] or epoxides [2] in the presence of acid catalysts has been well studied and is applied widely in industry [3]. On the other hand it is known that nitriles react with epoxides to give of oxazolines [4]; chiral oxazolines are formed in the case of chiral oxiranes [5]. Combination of the three reactants described above (activated aromatic compound, oxirane, and nitrile) leads to a qualitatively new result. As we have estimated, the reaction of 1,2- or 1,4-dimethoxybenzene with isobutylene oxide and nitriles RCN in concentrated sulfuric acid gives in good yield 1-R-6,7- or 1-R-5,8-dimethoxy-3,3-dimethyl-3,4-dihydroisoquinolines **1a-f** or (when R = CH_2COOEt) derivatives of tetrahydroisoquinolylideneacetic acid **2a,b** (we have called this reaction a "tandem alkylation-cyclization" reaction and it was described in the preliminary communication [6]).

The majority of the known methods of constructing the isoquinoline nucleus include the formation of the $C_{(4)}$–$C_{(4a)}$ or $C_{(1)}$–$C_{(8a)}$ bonds at the key stage [7]. In our method of obtaining substituted 3,4-dihydroisoquinolines these bonds are formed sequentially in "one-pot" without isolation of the intermediates. In the traditional syntheses of 3,4-dihydroisoquinolines by the Ritter reaction substituted styrenes [8] or benzylcarbinols [9] are used as precursors of the carbocation.

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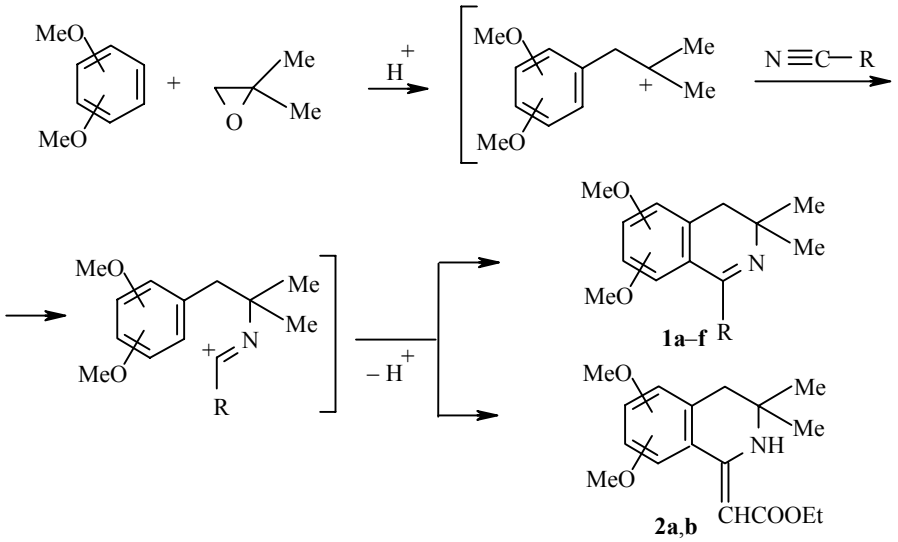
Scheme 1



1a-d, **2a** R = 6,7-$(MeO)_2$; **1a** R = Me, **b** R = SMe, **c** R = Ph, **d** R = CH_2Cl,
1e,f, **2b** R = 5,8-$(MeO)_2$; **1e** R = Me, **f** R = SMe

In our case the required carbocation is formed at the first stage of the process by acid-catalyzed alkylation of the activated aromatic compound. Subsequent electrophilic attack on the corresponding nitrile leads to an intermediate carbimmonium ion, which is cyclized to the substituted 3,4-dihydroisoquinoline **1** or the tetrahydroisoquinolylideneacetic acid ester **2**.

The reaction described is a simple and convenient one-reactor method of obtaining 1-substituted 3,3-dimethyl-3,4-dihydroisoquinolines with electron-donating substituents in positions 6,7 or 5,8 but it has some limitations. We were unable to carry out a reaction between 1,4-dimethoxybenzene and benzonitrile, probably because of steric hindrance arising between the phenyl ring in position 1 of the isoquinoline and the methoxy group in position 8. The tandem alkylation-cyclization reaction was also unsuccessful for such aromatic compounds as naphthalene (only traces of the desired products were formed), benzodioxole (a side reaction of of the dioxolane ring opening occurs), and thianthrene.

The analogous reaction with cyclohexene oxide is accompanied by rearrangement and substituted 3,3-tetramethylene-3,4-dihydroisoquinolines **3** or (6,7-dimethoxy-3,3-tetramethylene-1,2,3,4-tetrahydro-1-isoquinolylidene)acetic acid ester (**4**) are formed in low yields (3-12%) (see Scheme 2).

An increase in the reaction time to 12 h or a rise in temperature to 60-70°C did not lead to a larger yield. The desired compounds were isolated from the aqueous layer but only starting materials or polymeric products were detected in the organic layer.

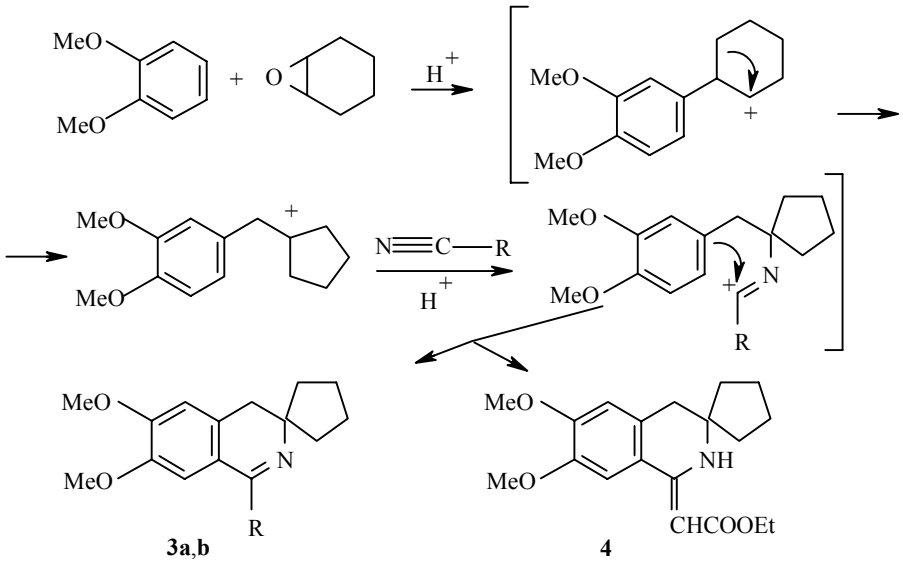
The composition of compounds **1-4** was confirmed by data of elemental analysis (Table 1), and the structure by IR and ^{1}H NMR spectra. Compounds **1a,c** were also obtained by the known route [9]. Compound **1b** was described previously in [10].

The IR spectra of the synthesized compounds (Table 2) revealed intense bands for the asymmetric and symmetric vibrations of the methoxy groups at 1265-1275 and 1030-1080 cm^{-1} respectively. The $\nu_{C=O}$ bands in the IR spectra of compounds **2a,b** and **4** were displayed at 1610-1630 cm^{-1} and had low intensity, which indicates the formation of an intramolecular hydrogen bond in the enamine form. The ^{1}H NMR data (Table 2) confirm the abovementioned. The position of the signals of the olefinic protons at 4.98-5.00 ppm for compounds **2a** and **4** proves *Z*-configuration for these compounds [16].

TABLE 1. Characteristics of the Synthesized Compounds **1-4**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
1a	$C_{14}H_{19}NO_2$	72.17 / 72.07	8.60 / 8.21	5.77 / 6.00	75-76 (hexane)	47
1c	$C_{19}H_{21}NO_2$	77.35 / 77.26	7.23 / 7.17	4.52 / 4.74	139-141 (acetone–ether)	55
1d	$C_{14}H_{18}ClNO_2$	61.95 / 62.80	6.44 / 6.78	5.37 / 5.23	100-103 (hexane)	47
1e	$C_{14}H_{19}NO_2$	72.57 / 72.07	8.44 / 8.21	5.73 / 6.00	37-39 (hexane)	35
1f	$C_{14}H_{19}NO_2S$	63.29 / 63.36	7.40 / 7.22	5.49 / 5.28	82-83 (MeOH+water)	35
2a	$C_{17}H_{23}NO_4$	67.19 / 66.86	7.38 / 7.59	4.92 / 4.59	104-105 (hexane)	80
2b	$C_{17}H_{23}NO_4$	67.05 / 66.86	7.64 / 7.59	4.29 / 4.59	Oil	72
3a	$C_{21}H_{23}NO_2$	79.05 / 78.47	7.08 / 7.21	4.31 / 4.36	90-92 (hexane–CH_2Cl_2)	3
3b	$C_{16}H_{21}NO_2S$	66.11 / 65.95	7.50 / 7.26	4.77 / 4.81	47-49 (MeOH)	6
4	$C_{19}H_{25}NO_4$	68.90 / 68.86	7.81 / 7.60	4.20 / 4.22	150-152 (ethanol)	12

Scheme 2



3a R = Ph, **b** R = MeS

The downfield shift of the =CH group signal in the ^{1}H NMR specrtum of compound **2b** (5.69 ppm) is probably due to the anisotropic influence of the 8-OMe group.

The anisotropic influence of the phenyl ring in position 1 of the isoquinoline in compound **1c** leads to highfield shift of the signals of the 7-MeO group (from 3.85 to 3.63 ppm) and of the 8-H (from 6.93 to 6.60 ppm, the signals of 5-H and 8-H coincide in $CDCl_3$).

TABLE 2. Spectral Characteristics of Compounds **1-4**

Com-pound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm				
		3.3-$(Me)_2$, 6H, s or $(CH_2)_4$, 8H, m	4-CH_2, s	H_{arom}	2-OMe s or two s	1-R
1a	1620, 1595, 1570, 1510, 1345, 1290, 1265, 1225, 1205, 1150, 1060, 980, 965, 835	1.13	2.55	6.58 (1H, s, 5-H); 6.93 (1H, s, 8-H)	3.84 (6H)	2.28 (3H, s, Me)
1c	1600, 1555, 1510, 1270, 1210, 1030	1.21	2.66	6.60 (2H, s, 5- and 8-H)	3.63 (3H, s); 3.87 (3H, s)	7.28-7.48 (5H, m, Ph)
1d	1605 (sh.), 1600, 1560, 1515, 1325, 1300, 1265, 1235, 1215, 1165, 1140, 1060, 985, 870, 850, 835	1.23	2.60	6.59 (1H, s, 5-H); 6.95 (1H, s, 8-H)	3.85 (6H, s)	4.45 (2H, s, CH_2Cl)
1e	1610, 1590, 1580, 1330, 1270, 1250, 1200, 1150, 1090, 1055, 1035, 970, 910, 800	1.09	2.48	6.83 and 6.97 (2H, two d, 6- and 7-H)	3.77 (3H, s); 3.82 (3H, s)	2.31 (3H, s, Me)
1h	1590, 1555, 1325, 1275, 1200, 1080, 1020, 1005, 980	1.19	2.53	6.75 (2H, d, 6- and 7-H)	3.72 (3H, s); 3.79 (3H, s)	2.28 (3H, s, MeS)
2a	3260 (NH), 1645, 1600, 1570, 1510, 1405, 1295, 1265, 1235, 1210, 1185 1150, 1040, 1005, 950, 870	1.21	2.69	6.55 (1H, s, 5-H); 7.06 (1H, s, 8-H)	3.83 (6H, s)	1.24 (3H, t, Me); 4.10 (2H, q, OCH_2); 4.98 (1H, s, CH); 8.81 (1H, br. s, NH)
2b	3250 (NH), 1600, 1505, 1305, 1270, 1175, 1090	1.15	2.69	6.72 (2H, s, 6- and 7-H)	3.67 (3H); 3.70 (3H)	1.20 (3H, t, Me); 4.05 (3H, q, OCH_2); 5.69 (1H, s, CH); 9.21 (1H, s, NH)
3a	1600, 1555, 1515, 1400, 1275, 1220, 1180, 1115, 1030, 1000, 960, 880, 845	1.61-1.90	2.72	6.68 (1H, s, 5-H); 6.87 (1H, s, 8-H)	3.63 (3H); 3.87 (3H)	7.40 and 7.55 (3H, m, and 2H, m, Ph)
3b	1595, 1565, 1510, 1275, 1215, 1200, 1135, 1110, 1040, 950, 860, 840	1.55-1.85	2.67	6.77 (1H, s, 5-H); 7.04 (1H, s, 8-H)	3.79 (3H); 3.83 (3H)	2.34 (3H, s, MeS)
4	3275 (NH), 1630, 1590, 1510, 1565, 1510, 1410, 1280, 1260, 1185, 1160	1.60-1.83	2.82	6.79 (1H, s, 5-H); 7.11 (1H, s, 8-H)	3.83 (6H)	1.25 (3H, t, Me);4.05 (2H, q, OCH_2); 5.00 (1H, s, CH); 9.07 (1H, s, NH)

Only one set of signals was registered in the ^{1}H NMR spectra of compounds **1,2** after the typical treatment. This indicates the regioselective opening of the epoxide ring under the reaction conditions. Cleavage of the oxirane at the least sterically hindered carbon atom was observed in the acid-catalyzed reaction of isobutylene oxide with phenetole [11], and an analogous mechanism would logically be proposed in the present case (route A). An alternative mechanism might be the reaction passing through the cyclopropylidenarenonium ion [12,13] (route B).

A quantum-chemical investigation of the formation of compound **2a** was carried out to specify the reaction pathway more precisely. This included calculation of the enthalpies of formation (ΔH_f) and the total energies (E_t) of this product and of possible intermediates of the process by the semiempirical MO LCAO using AM1 approximation [14] with full optimization of all the geometric parameters (see Scheme 3). The key stage in the classical Ritter reaction is the interaction of the carbocation with the nitrile [15]. The carbimmonium cation formed as intermediate is then cyclized in this case into dihydroisoquinoline **2a**.

The required carbimmonium cation I_6 may theoretically be formed by route A, one step of the latter is electrophilic attack of the $C_{(4)}$ atom of veratrole by 2-hydroxy-2-methyl-1-propyl cation (I_{1A}) (a possible product of the protonation of 2,2-dimethyloxirane). Subsequent deprotonation of the σ-adduct I_{2A} with the formation of the tertiary alcohol I_{3A}, O-protonation of the alcohol I_{3A}, and dehydration of cation I_{4A} leads to the tertiary cation I_{5A}. Interaction of the latter with ethyl cyanoacetate is bound to give the key intermediate I_6 which is converted by intramolecular attack into the σ-adduct I_7, and then into isoquinoline **2a**. The enthalpies of formation and the total energies of the possible intermediates and the reaction product are given in Scheme 3.

However it turned out that the protonation of 2,2-dimethyloxirane proceeds differently.

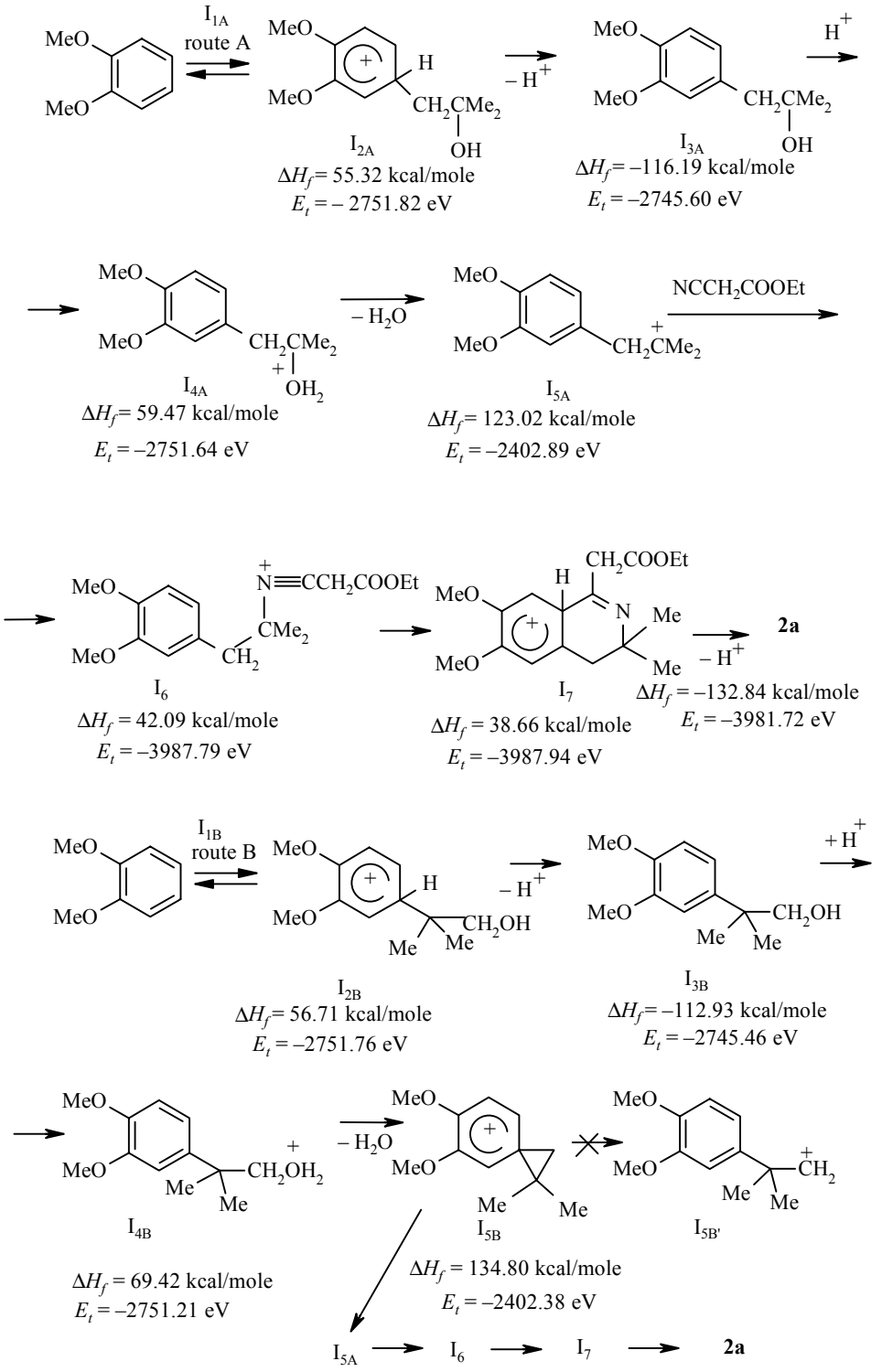
According to the calculations the attachment of proton to the oxygen atom results in cleavage of the $O_{(1)}$–$C_{(2)}$ bond and the formation of 1-hydroxy-2-methyl-2-propyl cation (I_{1B}) (see Scheme 4). Cation I_{1B} is far more stable than cation I_{1A} as follows from a comparison of the values of their enthalpies of formation and total energies. Detection of the oxonium cation (I_{1C}) on the potential energy surface of the reaction of 2,2-dimethyloxirane with proton was unsuccessful. All attempts to optimize I_{1C} geometry proved to be unsuccessful due to cleavage of the $O_{(1)}$–$C_{(2)}$ bond.

Since protonation of 2,2-dimethyloxirane leads to cation I_{1B} we have investigated the possibility of carrying out the alternative route (B) to obtain compound **2a**. The interaction of cation I_{1B} with veratrole should lead to the σ-adduct I_{2B} which is converted into 2-(3,4-dimethoxyphenyl)-2-methyl-1-propanol (I_{3B}). Protonation of alcohol I_{3B} gives hydroxonium cation I_{4B}. It turned out that splitting out of water from this cation occurs in a nonstandard manner. Cleavage of the C–O bond is accompanied by *ipso* attack of the aromatic ring by the electrophilic carbon atom leading to the phenonium cation I_{5B} and not to the primary carbocation $I_{5B'}$. The values of ΔH_f and E_t of the "supermolecule" $I_{5B} + H_2O$ were 70.57 kcal/mole and -2751.16 eV respectively and slightly exceed the analogous values for the intermediate I_{4B}. The minimum on the potential energy surface actually corresponds to intermediate I_{5B}. All the fundamental values of the Hess matrix were positive. The conversion $I_{5B} \rightarrow I_{5A}$ leads to a more stable cation and does not require significant energy consumption. The value of activation energy, estimated by the method of reaction coordinate was not greater than 2.2 kcal/mol. The length of the breaking C–C bond was accepted as the reaction coordinate. As follows from our calculations the conversion of the carbimmonium cation I_6 into the σ-adduct I_7 was also thermodynamically favorable, since the value of ΔH_f of the latter was less by 3.43 kcal/mole.

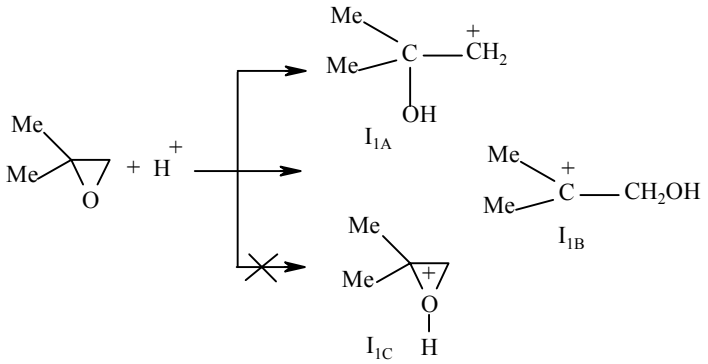
So pathway B seems the more probable of the two alternative routes to give 1-substituted 3,4-dihydroisoquinolines, since it assumes participation of the more stable electrophile, the 1-hydroxy-2-methyl-2-propyl cation (I_{1B}), in one of the first stages of the reaction. The value of ΔH_f of the "supermolecule" of veratrole + I_{1B} for a distance between the reaction centers of 3.00 Å was 75.13 kcal/mole, which is far less than the analogous value for the "supermolecule" veratrole + I_{1A} for the same interatomic distance (ΔH_f = 107.83 kcal/mole).

It seems probable that 1,4-dimethoxybenzene reacts under the present conditions by the same mechanism as veratrole leading to compounds **1e,f,2b**. In any case the mechanism of this reaction requires further study and refinement.

Scheme 3


I1A
route A
MeO
MeO
H
CH2CMe2
OH
I2A
ΔHf = 55.32 kcal/mole
Et = – 2751.82 eV
– H+
H+
I3A
ΔHf = –116.19 kcal/mole
Et = –2745.60 eV
– H2O
I4A
ΔHf = 59.47 kcal/mole
Et = –2751.64 eV
NCCH2COOEt
I5A
ΔHf = 123.02 kcal/mole
Et = –2402.89 eV
N≡CCH2COOEt
CMe2
CH2
I6
ΔHf = 42.09 kcal/mole
Et = –3987.79 eV
CH2COOEt
N
Me
I7
ΔHf = 38.66 kcal/mole
Et = –3987.94 eV
2a
ΔHf = –132.84 kcal/mole
Et = –3981.72 eV
I1B
route B
CH2OH
I2B
ΔHf = 56.71 kcal/mole
Et = –2751.76 eV
+H+
I3B
ΔHf = –112.93 kcal/mole
Et = –2745.46 eV
CH2OH2
I4B
ΔHf = 69.42 kcal/mole
Et = –2751.21 eV
I5B
I5B'
ΔHf = 134.80 kcal/mole
Et = –2402.38 eV
I5A
I6
I7
2a

Scheme 4



I_{1A} ΔH_f = 166.84 kcal/mole, E_t = -947.25 eV;
I_{1B} ΔH_f = 131.75 kcal/mole, E_t = -948.93 eV

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument for nujol suspensions and in a thin film (**2b**). The ^{1}H NMR spectra were obtained at 25°C on Tesla BS-587A (80 MHz) (in $CDCl_3$) and Bruker WM-250 (250 MHz) (for compounds **1e,3a,b,4** in DMSO-d_6) spectrometers, using HMDS as internal standard. A control over the path of reactions and the purity of the products obtained was carried out by TLC on Silufol in the system chloroform–acetone, 9 : 1, visualization was carrying by a 3% solution of chloranil in toluene. Quantum-chemical calculations were carried out on a Pentium 133 computer with the MOPAC 7.0 program package [17].

(6,7-Dimethoxy-3,3-dimethyl-1,2,3,4-tetrahydro-isoquinolylidene)acetic Acid Ethyl Ester (2a). A solution of veratrole (13.8 g, 0.1 mol), isobutylene oxide (9.9 ml, 0.1 mol), and cyanoacetic ester (10.7 ml, 0.1 mol) in toluene (10 ml) was added dropwise during 30 min to conc. H_2SO_4 (55 ml), maintaining the temperature of the mixture at 20-30°C. The reaction mixture was stirred for 2 h at 20°C, poured into water (300 ml), the organic layer was separated, and washed with water (40 ml). The combined aqueous layers were washed with toluene (30 ml × 2) alkalized with ammonium carbonate, then with aqueous ammonia to pH ~8, extracted with ether, and the extract dried over $MgSO_4$. After distillation of the ether the residue was treated with cold methanol, crystallized from hexane, and product **2a** was obtained. Products **1b,c** were synthesized analogously from veratrole and methyl thiocyanate or benzonitrile respectively. Products **1f,2b** were synthesized from 1,4-dimethoxybenzene and methyl thiocyanate or cyanoacetic ester. Compound **1b** had mp 64-65°C (from alcohol), ref. [10] mp 64-65°C. Compound **2b** was decarboxylated on heating above 120°C, consequently it was purified by column chromatography on silica gel, eluent being ethyl acetate–hexane 5 : 1.

6,7-Dimethoxy-1,3,3-trimethyl-3,4-dihydroisoquinoline (1a) was obtained from veratrole analogously to compound **2a**. After reaction completion the acidic aqueous layer was diluted twofold with water. Then for hydrolysis with subsequent decarboxylation [9] of the ester **2a,** the layer was heated under reflux for 2-4 h, until the spot of compound **2a** dissapeared (by TLC)**,** and then processed as described above. After distillation of the ether, the residue was redistilled in vacuum, collecting the fraction of bp 148-150°C/12 mm Hg, which then was crystallized. Compound **1e** was synthesized similarly from 1,4-dimethoxybenzene and cyanoacetic ester.

1-Chloromethyl-6,7-dimethoxy-3,4-dihydroisoquinoline (1d) and Its Hydrochloride (1d·HCl). A solution of veratrole (13.8 g, 0.1 mol), isobutylene oxide (7.2 g, 0.1 mol), and chloroacetonitrile (7.6 g, 0.1 mol) in toluene (50 ml) was added dropwise during 40 min to conc. H_2SO_4 (45 ml) (20-40°C, cooling with a water bath). The reaction mixture was stirred for 2 h, poured into cold water (300 ml), the organic layer was separated, and the aqueous layer extracted with toluene (50 ml). The aqueous layer was alkalized to pH ~7 and

extracted with *tert*-butyl methyl ether (150 ml × 2). The extract was dried over magnesium sulfate, three quarters of the solvent was distilled off, the residue was diluted with hexane (200 ml), the precipitate was recrystallized from hexane (200 ml) in cold (-20°C), and compound **1d** (12.0 g) in 47% yield was obtained as coarse light brown crystals, mp 100-103°C. The substance was stable in the air for several weeks, but on contact with ammonia or alkali rapidly dimerized to a dark red pyrazino[2,1-*a*:5,4-*a*']diisoquinoline derivative [18]. Partial dimerization also takes place on isolating compound **1d**, which reduces its yield. The hydrochloride salt **1d**. HCl was obtained by passing dry HCl through a solution of **1d** base in toluene, yield 85%; mp 191-193°C (2-propanol–ether). IR spectrum (nujol), cm^{-1}: 1630, 1600, 1550, 1510, 1330, 1275 ($\nu_{as\ C-O-C}$), 1245, 1220, 1150, 1060 ($\nu_{s\ C-O-C}$), 1035, 995, 870, 860 (the NH group was not observed in the IR spectrum due to the formation of hydrogen bonds). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.56 (6H, s, Me); 3.00 (2H, s, 4-CH_2); 3.93 (3H, s, OMe); 3.98 (3H, s, OMe); 5.29 (2H, s, CH_2Cl); 6.82 (1H, s, 5-H); 7.36 (1H, s, 8-H); 14.85 (1H, br. s, NH).

1-(6,7-Dimethoxy-3,3-tetramethylene-1,2,3,4-tetrahydroisoquinolylidene)acetic Acid Ethyl Ester (4). A solution of veratrole (12.8 ml, 0.1 mol), cyclohexene oxide (10 ml, 0.1 mol), and ethyl cyanoacetate (10.7 ml, 0.1 mol) in toluene (80 ml) was added dropwise during 0.5 h to conc. H_2SO_4 (50 ml) (20-60°C). The reaction mixture was stirred for 2 h, poured into cold water (300 ml), the organic layer was separated, the aqueous layer was extracted with toluene (40 ml), and then neutralized with ammonium carbonate to pH ~7. The precipitate was separated, washed with water, dried, and crystallized from 2-propanol, to give compound **4** (3.03 g, 9%); mp 150-152°C. Compound **3a** was obtained similarly but the oily substance formed after alkalization was extracted with hot hexane (50 ml × 2). After distillation of the hexane the residue was crystallized from a hexane–CH_2Cl_2, 5 : 1 mixture. Compound **3a** (0.9 g, 3%) was obtained.

6,7-Dimethoxy-1-methylthio-3,3-tetramethylene-3,4-dihydroisoquinoline (3b) was obtained analogously to compound **4** from veratrole (12.8 ml, 0.1 mol), cyclohexene oxide (10 ml, 0.1 mol), methyl thiocyanate (6.9 ml, 0.1 mol) in toluene (70 ml) and conc. H_2SO_4 (50 ml). The reaction mixture was stirred for 6 h at 25°C. The neutralized aqueous layer was extracted with CH_2Cl_2 (2 × 40 ml), the extract washed with water, and dried over $MgSO_4$. After distillation of the solvent the residue was crystallized from methanol by cooling to -15°C. Compound **3b** (1.9 g, 6%) was obtained.

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