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Synthesis of Chiral Benzacridone Derivatives by Three-Component Condensation

S. S. Koval'skaya, N. G. Kozlov, and E. A. Dikusar

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus
Minsk, 220072 Belarus
e-mail: loc@ifoch.bas-net.by

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Abstract—A three-component condensation of (2-bornylidene)acetaldehyde and 2-naphthylamine with various, in particular, dissymmetrical, cyclic β-diketones afforded derivatives of 12-(2-bornylidene)methyl-8,9,10,12-tetrahydro-7H-benzo[*a*]acridin-11-one containing in the structure three and more asymmetrical carbon atoms. Steric factors govern the prevailing formation of (12*R*)-isomers of benzacridones (*R*/*S*H ≈ 7 : 5) and the orientation of the substituents of the cyclohexenone fragment. These factors ensure also the regiospecificity of the reaction leading exclusively to the formation of 8,9-disubstituted benzacridones at the use of 4,5-disubstituted cyclohexane-1,3-diones.

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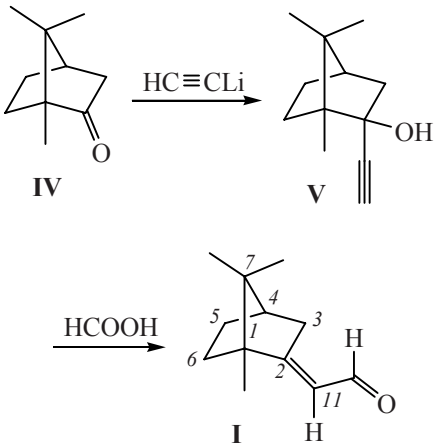
Reactions of cascade heterocyclization (cyclocondensation) involving aromatic aldehydes, amines, and cyclic β-diketones are convenient procedure for the synthesis of derivatives of benzo[*a*]acridine, 4,7-phenanthroline and other fused azaheterocycles [1–3]. The compounds obtained in these reactions are endowed with a number of useful properties, in particular, a versatile biological activity [4–6]. The data on cyclocondensation involving nonaromatic aldehydes are scarce. The rare examples of a successful synthesis correspond to the reactions with formaldehyde involvement [7–9]. This fact apparently is due to the tendency of aliphatic aldehydes to oxidation and autocondensation.

In this study we investigated for the first time a three-component condensation of (2-bornylidene)-acetaldehyde (**I**) and 2-naphthylamine (**II**) with various cyclic β-diketones **III**. The expediency of the use in this reaction of aldehyde **I** was dictated by several reasons. The considerable spatial screening of the α,β-unsaturated fragment in this compound decreases the opportunity of side reactions, e.g., of polymerization, and the chirality of aldehyde **I** makes it possible to synthesize chiral azaheterocyclic derivatives; therewith at the use of dissymmetrical (containing asymmetrical or enantiotopic carbon atoms) β-diketones the diastereomers might form with unlike probability.

Initial (2-bornylidene)acetaldehyde (**I**) we synthesized in two stages from camphor (**IV**). The synthesis of 2-ethynylisoborneol (**V**) by treating ketone **IV** with lithium acetylenide we described formerly [10]. The Meyer–Schuster rearrangement [11] of compound **V** under the treatment with formic acid with a high selectivity resulted in α,β-unsaturated aldehyde **I**. The structure of this compound was established from the data of IR and ^{1}H NMR spectroscopy. The IR spectrum contains a band at 1680 cm^{-1} characteristic of the vibrations of an aldehyde group conjugated with a double bond. The frequency of the band of the C=C bond 1640 cm^{-1} and also its integral intensity many times lower than that of the aldehyde group band indicate the *s-trans*-configuration of the α,β-unsaturated fragment of (2-bornylidene)acetaldehyde. This configuration was also confirmed by the ^{1}H NMR spectral data: the vicinal coupling constan of the aldehyde (δ 9.84 ppm, doublet) and olefin (δ 5.79 ppm, doublet of triplets) protons equals 8 Hz corresponding to their transoid orientation. The involvement of the olefin proton in two other couplings (2.4 Hz) corresponding to the *trans*-allyl coupling with the protons at the C^3 atom



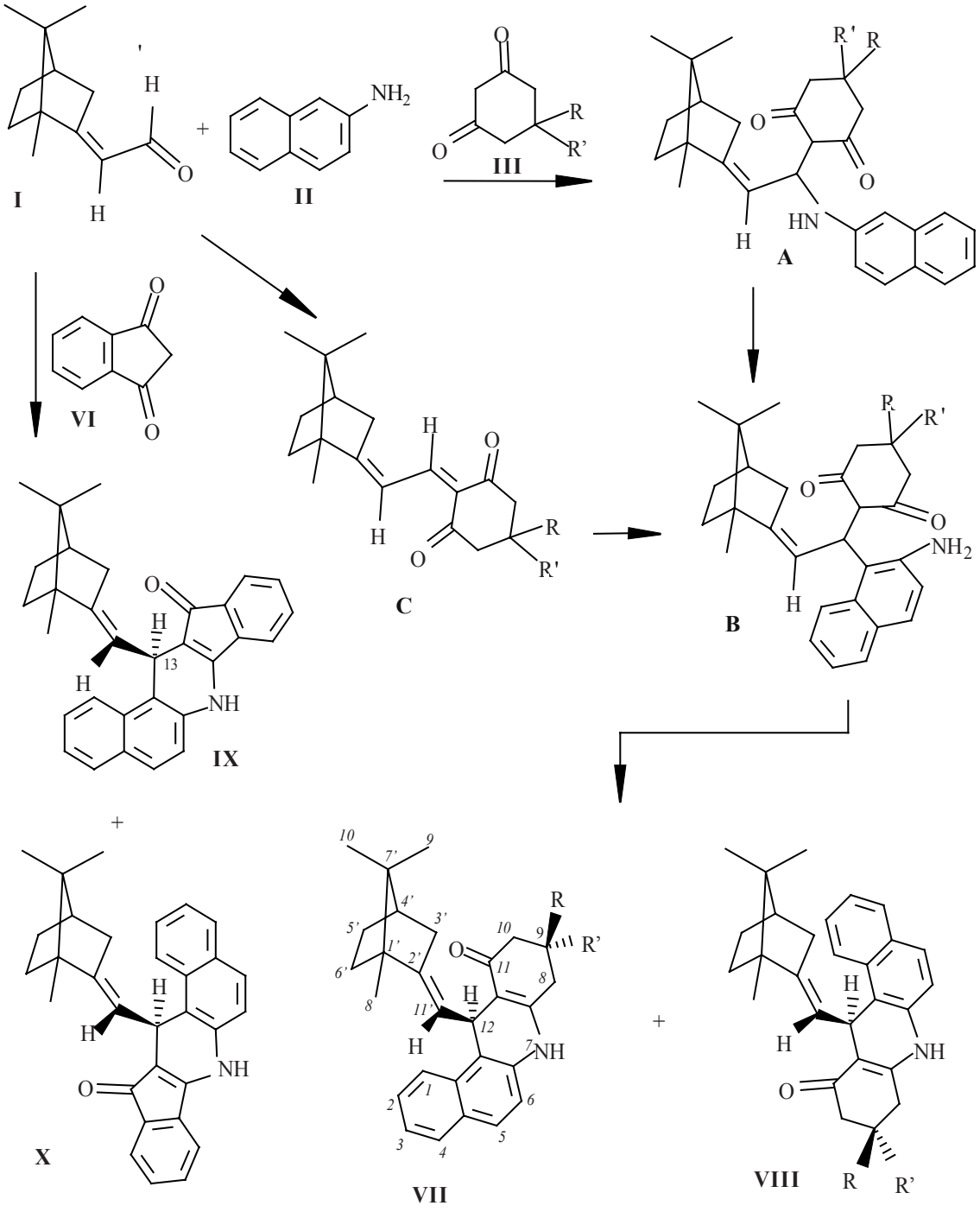
of camphane skeleton indicates the *trans*-configuration of the semicyclic double bond. Therefore (2-bornylidene)acetaldehyde (**I**) formed as a result of the Meyer–Schuster rearrangement from the 2-ethynylisoborneol is an individual *trans-s-trans*-isomer. This spatial arrangement of compound **I** is well consistent both with thermodynamic factors (greater stability of *trans*-isomers) and with the sterical requirements (maximum remoteness of the bulky substituents).

The three-component condensation of (2-bornylidene)acetaldehyde (**I**), 2-naphthylamine (**II**), and cyclic β-diketones [cyclohexane-1,3-dione (**IIIa**), its derivatives **IIIb–IIIg**, or indanedione (**VI**)] was carried out along common procedure: by boiling equimolar amounts of reagents in ethanol [12]. The formed benzacridones were precipitated from the reaction mixture by ethyl ether. By repeated recrystallization of stereoisomers mixture from acetone, ethanol and/or its mixture with benzene we isolated samples for spectral investigation.

The reactions of (2-bornylidene)acetaldehyde and 2-naphthylamine with β-diketones lacking asymmetrical or enentiotopic carbon atoms [cyclohexane-1,3-dione (**IIIa**), dimedone (**IIIb**) or indanedione (**VI**)] led to the formation of mixtures of the corresponding stereoisomeric azaheterocycles of different configurations (*R* or *S*) of the asymmetrical atom C^{12}. Cyclohexane-1,3-dione and dimedone yield mixtures of (12*R*)-isomers **VIIa, VIIb** and (12*S*)-isomers **VIIIa, VIIIb** in a ratio ~7 : 5. In the reaction with the indanedione the (12*R*)- and (12*S*)-isomers **IX** and **X** formed in materially equal amounts.

The structure of compounds obtained was deduced from IR and ^{1}H NMR spectra. The IR spectra of compounds **VII** and **VIII** contain several bands in the region 3200–3450 cm^{-1} belonging to the NH group vibrations, and also 2 bands with the wavenumber ~1595 and 1580 cm^{-1} characteristic of vibrations of a conjugated ketoenamine fragment ("amide vinylog"). The spatial arrangement of the synthesized benzacridones was established from the data of ^{1}H NMR spectroscopy. The NMR spectra were registered on the samples enriched with the corresponding isomer up to 80% or more. DMSO-d_6 was used as a solvent for the formed in the reaction azaheterocyclic derivatives are virtually insoluble in the other deutereted solvents. In many events the proper signals of the solvent (δ 2.50 and ~3 ppm) overlapped (totally or partially) the proton signals required for the estimation of the spatial arrangement of the analyzed compound. This difficulty was overcome by a simple trick: to the solution of the compound in DMSO several drops was added of D_2O or CCl_4. As a result both the signals of the solvent (δ 3 ppm) and the solute slightly shifted (downfield or upfield) and thus the multiplicity of the overlapped signal was revealed. The assignment of signals was based on the multiplicity, and in case of the coincidence, on the data of the double resonance.

The spectra of dimedone derivatives **VIIb** and **VIIIb** contain the simplest set of signals. Due to the significant spatial shielding the semicyclic double bond of the (2-bornylidene)acetaldehyde is not involved into the reaction and retains its *trans*-configuration as confirmed by the presence of a *trans*-allyl coupling between the protons attached to atoms $C^{3'}$ and $C^{11'}$ ($^4J \approx 2$ Hz). The value of the vicinal coupling constants for protons at the atoms $C^{11'}$ and C^{12} (δ ~ 4.8 and ~5.1 ppm respectively) in both stereoisomers attains 9.6 Hz indicating that their reciprocal position is close to *anti*-periplanar. Thus the stereoisomeric compounds **VII** and **VIII** are differ by the mutual orientation of camphane and benzacridone rings: In one of isomers to the *gem*-dimethyl bridge is directed the cyclohexenone, in the other, naphthalene fragment of the heterocycle. The difference in the shielding properties of these moieties allows unambiguous conclusions on the spatial arrangement of compounds obtained. In the spectrum of the major isomer of the mixture was identified a signal of proton $H^{3'}$-*exo* looking like a broadened doublet of doublets (^2J 16, $^3J_{3'\text{-exo},4'}$ 4, $^4J_{3''\text{-exo},5'\text{-exo}} = {}^4J_{3'\text{-exo},11'} \approx 2$ Hz). The chemical shift of this proton 3.01 ppm indicated the proximity of the proton to the carbonyl group and testified to the structure of (12*R*)-isomer **VIIb**. The signal of the geminal proton $H^{3'}$-*endo* appeared at δ 2.12 ppm (doublet, ^2J 16 Hz). The signals of the corresponding pair of the geminal protons of (12*S*)-stereoisomer **VIIIb** had analogous multiplicity and appeared at 2.61 ($H^{3'}$-*exo*) and 2.66 ppm ($H^{3'}$-*endo*).



III, R = R' = H (**a**), CH_3 (**b**); R = Ph, R' = H (**c**); **VII, VIII**, R = R' = H (**a**), CH_3 (**b**); R' = Ph, R = H (**c**); R = Ph, R' = H (**d**).

The change in the spatial surrounding compared to isomer **VII** resulted in an upfield shift of the signal of the *exo*-proton at the atom $C^{3'}$ ($\Delta\delta$ –0.4 ppm), and of the signal of the *endo*-proton, on the contrary, downfield ($\Delta\delta$ 0.55 ppm). Benzacridone ring had a significant shielding influence on the camphane ring, and therefore the signals of many protons were observed in abnormally strong field. For instance, the methyl groups 1-CH_3 and 7-CH_3-*syn* in the spectrum of compound **VIIb** appeared at δ 0.47 and 0.59 ppm respectively, and in the spectrum of stereoisomer **VIIIb**, at 0.51 ppm (6H). The signals of *endo*-protons at the atoms C^{52} and C^{62} look like double

doublets of doublets with the chemical shifts 1.12 and 0.92 ppm (^2J 12.0, $^3J_{endo,endo}$ 8.0, $^3J_{endo,exo}$ 4.0 Hz) (**VIIb**), 0.99 and 0.95 ppm, the same coupling constants (**VIIIb**). The position and multiplicity of the rest signals are well consistent with the assumed structure of the compounds (see EXPERIMENTAL).

We established formerly that two geminal protons of the cyclohexenone ring of benzacridones located in the α-position to the carbonyl group possessed larger coupling constant (18 Hz) than the protons contiguous to the double bond. This conclusion was based on the findings that the oximation of the carbonyl group led to the downfield shift (Δδ ≈ 0.6–0.7 ppm for pseudoequatorial, 0.2–0.3 ppm for pseudoaxial protons) just of the proton signals with the large coupling constant. The position of signals of the second pair of protons therewith remained practically unchanged. In their turn the chemical shift values of protons at the atoms C^8 and C^{10} of the benzacridone ring depend on the shielding properties both of the substituents in the cyclohexenone ring and the substituents at the atom C^{12}, and this values can vary in a fairly wide range. In the stereoisomeric compounds **VIIb** and **VIIIb** the signals of the geminal protons adjacent to the carbonyl group attached to the atom C^{10} of the dimedone fragment were observed downfield (δ ≈ 2.45 and 2.30 ppm, J 18.0 Hz) with respect to the two geminal protons at the atom C^8 (δ 2.28 and ~2.00 ppm, J 16.0 Hz). These data we used in the analysis of the structure of benzacridone derivatives of more complex structure (see below).

We discussed the mechanism of the theree-component cyclocondensation more than once [13]. The most probable route seems the proceeding of the reaction through the stage of Mannich base **A** formation that via retrohydride rearrangement can transform into intermediate **B**. The cyclization of the latter leads to the formation of compound **VII** or **VIII**. The intermediate **B** can presumably form also at alkylation of 2-naphthylamine by the product of crotone comdensation of aldehyde **I** and β-diketone **III**, diketodiene **C** But we believe that the involvement of the latter is hardly possible for the significant difference in the sterical accessibility of the α- and β-sides of intermediate **C** should have resulted in a higher stereoselectivity of alkylation and consequently to a higher fraction of (12*R*)-stereoisomer in the reaction mixture. Some excess in the mixture of benzacridones (12*R*)-isomers **VII** in the syntheses with cyclohexane-1,3-dione (**IIIa**) or dimedone (**IIIb**) is governed apparently by moderate preference of intermediates **A** formation where the larger fragments of the molecule, the camphane and the naphthyl, and maximally removed from each other. In the reaction with indanedione whose molecule is bulky, on the contrary, a slight (52%) prevalence of (13*S*)-isomer **X** was found in the reaction mixture. In event of the reaction proceeding through the stage of intermediate **C** formation this would mean that the molecule of the naphthylamine predominantly added from the side shielded by the *gem*-dimethyl bridge of the camphane skeleton.

The reaction involving 5-phenylcyclohexane-1,3-dione (phendione) (**IIIc**) containing an enantiotopic carbon atom led to the formation of four stereoisomeric products differing not only in the mutual orientation of the camphene and benzacridone fragments but also in the spatial orientation of the phenyl substituent with respect to the former one. Proceeding from the data of ^{1}H NMR spectroscopy the stereoisomer prevailing in the reaction mixture (~44%) was assigned the structure of (12*R*,9*R*)-isomer **VIIc**. The conclusion on the (*R*)-configuration of atom C^{12} was based on the same criteria: downfield shift of the signal of the *exo*-proton at the atom $C^{3'}$ of this compound (δ 3.20 ppm) indicated its spatial proximity to the carbonyl group of the benzacridone fragment. The 9*R* configuration was assigned to this compound because the signal of the proton at the atom C^9 contiguous to the phenyl substituent appeared in somewhat stronger field (δ 3.47 ppm) than in the spectrum of its isomer **VIId** (see below) indicating that it occurred in the field of shielding from the bornylidene fragment corresponding to the *trans*-location of the camphene and phenyl substituents in this compound. In compound **VIId** stereoisomeric with respect to atom C^9 (~15% in the mixture) the signal of the corresponding proton appeared at 3.92 ppm. In the pair of (12*S*)-isomers the chemical shifts of protons H^9 have closer values: 3.47 ppm for the *trans*-isomer **VIIIc** (~31%) and 3.64 ppm for the *cis*-isomer **VIIId** (~10% in the mixture) since the cyclohexenone fragment of this compound is turned to the opposite direction and is less affected by the shielding effect of the camphene ring.

In the spectra of compounds stereoisomeric with respect to atom C^9 the signal of proton H^9 possesses different multiplicity. In the spectra of *trans*-isomers **VIIc** and **VIIIc** the signal appears like a quintet, and all its vicinal constants equal ~6 Hz. This value of the coupling constant intermediate between the axial-pseudoaxial (~9 Hz) and axial-pseudoequatorial value (~4 Hz) testifies that in the cyclohexenone fragment all bond angles are distorted to a great extent, therefore the conformation with the equatorially oriented phenyl group fails to be

thermodynamically preferable, and the conformational equilibrium results in the appearance of the average value of the coupling constants. In the *cis*-isomers of benzacridones **VIId** and **VIIId** the corresponding signals look like triplet of triplets with the constants 9 and 4 Hz. The first constant corresponds to the axial-pseudoaxial coupling of the proton H^9 with the pseudoaxial protons at the atoms C^8 and C^{10} indicating the equatorial orientation of the phenyl substituent in these isomers. Evidently the conformers with the axially oriented phenyl are unfeasible for the *cis*-isomers due to the nearer position to the camphene fragment than at the phenyl's equatorial orientation. Hence the different multiplicity of the signal of proton attached to C^9 also indirectly confirms that the minor component in each pair of (12*R*)- or (12*S*)-isomers is 9,12-*cis*-isomer.

In the cyclization with phendione (**IIIc**) also predominantly formed (12*R*)-stereoisomers, and their ratio to (12*S*)-isomers was materially the same as for compounds **VIIa, VIIb** and **VIIIa, VIIIb**: the fraction of compounds **VIIc, VIId** amounted to 59%. Whereas the ratio of stereoisomers with respect to atom C^9 was for both pairs of (12*R*)- and (12*S*)-isomers ~3:1 with the prevalence of *trans*-isomers. Evidently, intermediate **B**, precursor of the cyclization stage, existed predominantly in a conformation where the phenyl group was directed to the side opposite to the camphane fragment governing the prevailing formation in the reaction of 9,12-*trans*-isomers.

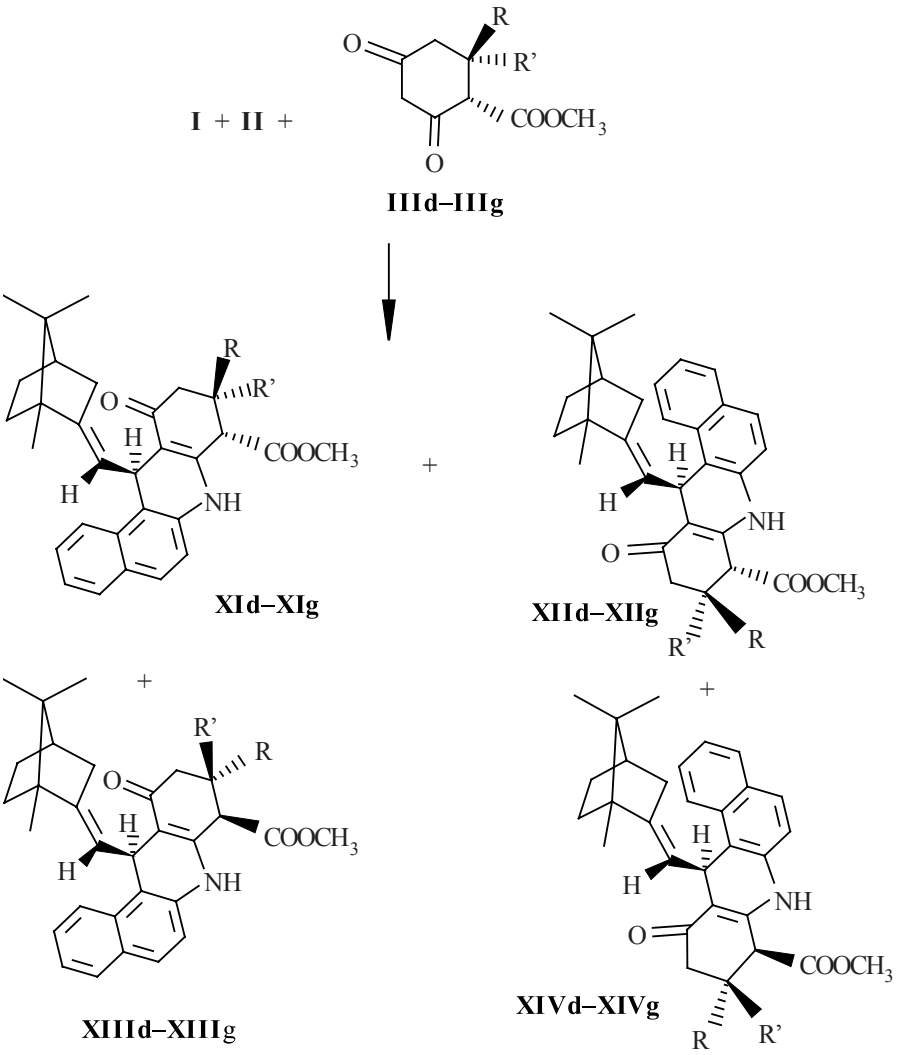
Stereochemical control is also observed in the reaction involving 4-methoxycarbonylcyclohexane-1,3-diones with various substituents at the C^5 atom **IIId–IIIg**. Compound **IIId** like phendione furnished by the reaction a mixture of four stereoisomers **XId–XIVd** with the fractions in the reaction mixture equal to 42, 33, 17, and 8% respectively.

The structure of the appropriate stereoisomer was assigned to each component of the reaction mixture based on the same criteria as in the case of phendione derivatives: The chemical shift of proton H^{32} -*exo* ~3 ppm in isomers **XId** and **XIIId** indicated the spatial nearness of these protons to the carbonyl group and testified to the (12*R*)-configuration of the respective compounds. The signals of *endo*-protons at the atom $C^{3'}$ appeared at 2.14 and 2.12 ppm respectively. In the spectra of (12*S*)-isomers **XIId** and **XIVd** the corresponding signals were observed at 2.65 and 2.54 ppm ($H^{3'}$-*exo*), 2.52 and 2.48 ppm ($H^{3'}$-*endo*). The conclusions on the orientation of the ester group in each of the isomers, like in the case of above cited phendione derivatives, were made based on the chemical shift of protons at the atom C^8. In compounds **XId** and **XIId** the corresponding singlet signals appeared upfield (3.04 and 3.09 ppm respectively) with respect to those of compounds **XIIId** and **XIVd** (3.29 and 3.31 ppm) due to the shielding by the camphane fragment in the first two compounds and indicating the 8,12-*trans*-position of the substituents therein.

As seen from the data presented, in the course of the reaction occurred the preferable formation of (12*R*)-isomers and also isomers with the *trans*-location of the camphene and the ester substituents (**XId** and **XIId**). The slightly different isomers ratio from that observed with phendione **IIIc** originates not from the sterical distinctions but rather from the stoichiometric conditions of the reaction: Since iintial β-diketone **IIId** is a racemate, the fraction of isomers with the (*S*)-configuration of atom C^8 (**XId** + **XIVd**) should be equal to the fraction of isomers with the (*R*)-configuration of the same atom (**XIId** + **XIIId**).

The heterocyclization may result both in the formation of 8- and 10-methoxycarbonyl derivatives **XV** or **XVI**.

The structure of 8-methoxycarbonyl derivatives was assigned to compounds **XId–XIVd** because in the spectra of all four isomer appeared two doublet signals with the geminal coupling constant 18 Hz characteristic, as mentioned above, for the protons linked to the atom C^{10}. The observed chemical shifts of the signals of these protons are well consistent with the structure of 8-methoxycarbonyl derivatives. In the spectra of analogs **VIIb** and **VIIIb** lacking the ester group the signals of the corresponding protons appeared at 2.45 and 2.30 ppm. The upfield signal belongs apparently to the proton located in the *cis*-position with respect to the camphene fragment and occurring in the shielding field of the latter. In the spectrum of compounds **XI** the signals of these protons were observed at 2.78 and 2.31 ppm. Obviously the signal of proton H^{10}-*trans* shifted downfield (Δδ 0.33 ppm) due to 1,3-nonbonding interaction with the polar ester group. The signal of proton H^{10}-*cis* whose spatial surrounding is virtually identical in compounds **VIIb** and **XId** nearly did not shift. The same relations in the chemical shifts was observed also in the spectrum of the second *trans*-isomer, compound **XII**. In the spectrum of *cis*-isomer **XIII** the signals of protons attached to C^{10} had chemical shifts 2.64 and 2.46 ppm. Obviously, in this case the signal of the *cis*-directed proton shifted downfield for it was deshielded by the *cis*-methoxycarbonyl group (Δδ 0.34 ppm). The chemical shift of the proton H^{10}-*trans* (2.46



R = R' = CH_3 (**d**); R' = H, R = 2,4,6-$(CH_3)_3C_6H_2$ (**e**), 3,4-$(CH_3O)_2C_6H_3$ (**f**), 3,4-$(OCH_2O)C_6H_3$ (**g**).

ppm), on the contrary, was the same as in the spectrum of analog **VIIb** (2.45 ppm). The chemical shifts of the protons of the second *cis*-isomer **XIVd** are very close to the signals of compound **XIIId**.

The formation of 8-methoxycarbonylregioisomers corresponds to the cyclization of intermediate **B** at the sterically less accessible (shielded by the ester substituent) carbonyl group of the β-diketone. Nonetheless, no 10-regioisomers were detected in the reaction mixture. Evidently the formation of conformers with the spatially close camphane fragment and ester group necessary for obtaining 10-regioisomers required strong sterical hindrances, and therefore the cyclization proceeded regiospecifically.

The heterocyclization involving 5-aryl-4-methoxycarbonylcyclohexane-1,3-diones **IIIe–IIIg**, racemic compounds with the *trans*-location of the ester and aryl substituents, also led to the formation of four stereoisomer **XI–XIV** whose weight fraction in the reaction mixture reached ~26, 18, 32, and 24% respectively. The structure of the corresponding stereoisomers was assigned to compounds obtained in the same way as described before based on the comparison of the chemical shifts of protons at the key carbon atoms C^{32}, C^{8}, and C^{9}. The structure of (12*R*)- or (12*S*)-isomers was ascribed to the compounds obtained proceeding from the chemical shifts of the protons at the atom $C^{3'}$ of the camphene skeleton (see above). Compounds **XIIIe–XIIIg** and **XIVe–XIVg** whose spectra contained the signal of the proton at the atom C^{9} linked to the aromatic substituent in a stronger field ($\delta \approx 4.0$ ppm) were assigned the structure of isomers with the *trans*-location of the aryl substituent with respect to camphane fragment. In the *cis*-isomers **XIe–XIg** and

XIIe–XIIg the corresponding signal was not shielded by the alicyclic fragment and appeared un the region 4.25 ppm. The signal of methine proton at the atom C^8 in compounds **XIIIe–XIIIg** and **XIVe–XIVg** appeared downfield ($\delta \approx 33.6$ ppm) from the signals of isomers **XIe–XIg** and **XIIe–XIIg** with the *trans*-directed methoxycarbonyl group ($\delta \approx 3.3$ ppm).

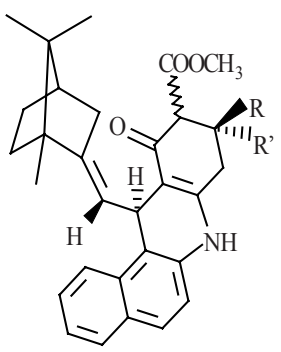
As seen from the described isomers ratio in the reaction mixture the reaction with 5-aryl-4-methoxycarbonylcyclohexane-1,3-diones afforded predominantly (12*R*)-isomers [(**XI**) +(**XIII**) 58% in the mixture], whereas the fraction of the *trans*- and *cis*-isomers in the reaction mixture did not differ as significantly as in the case of phendione or methoxycarbonyldimedone derivatives. This fact is due to the spatial structure of initial β-diketones. Inasmuch as in compounds **IIIe–IIIg** the aryl and ester substituents had a reciprocal *trans*-orientation, the benzacridone isomer with the *trans*-directed aryl substituent necessarily possessed a *cis*-directed methoxycarbonyl group, and vice versa. As a result the stereoselectivity with respect to chiral centers C^8 and C^9 was low, and the isomers with the *trans*-directed aryl substituent were a little more numerous.

In all stereoisomeric 9-aryl-8-methoxycarbonylbenzacridones **XIe–XIg–XIVe–XIVg** the signals of protons at the atoms C^8 and C^9 have the multiplicity corresponding to their axial (pseudoaxial) orientation (see EXPERIMENTAL). Evidently the existence of these compounds in the form of axial-pseudoaxial conformer is unfavorable due to the spatial closeness of the camphane fragment and one of substituents attached to atoms C^8 or C^9.

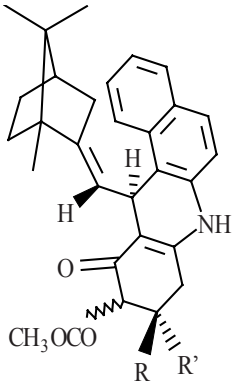
Thus the three-component condensation of (2-bornylidene)acetaldehyde with 2-naphthylamine and cyclic β-diketones made it possible to synthesize 12-(2-bornylidene)methyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one with versatile substituents in the cyclohexenone ring. The reaction is regiospecific and moderately stereoselective due to the different stability of various conformers of the aminodiketone intermediate whose formation precedes the cyclization stage.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer Nicolet Protégé-460. ^{1}H NMR spectra were registered on a spectrometer Bruker Avance (500 MHz) from solutions in $CDCl_3$ or DMSO-d_6, internal reference TMS. The reaction progress was monitored and the composition of products was checked by GLC on a chromatograph Chrom-5 equipped with a glass column 2000×2 mm packed with a carrier Chromaton-N-AW-DMCS (0.16–0.20), liquid phase Apiezon L.



XV



XVI

(2-Bornylidene)acetaldehyde (I). In 50 ml of conc. HCOOH was dissolved 8.9 g (50 mmol) of 2-ethynylisoborneol (**V**) prepared by procedure [10], and the solution was boiled till the completion of the reaction (~2 h, GLC monitoring). The reaction mixture was diluted with 300 ml of water, cautiously neutralized with aqueous ammonia, the reaction products were extracted by an organic solvent. The best results were obtained at extraction with hexane, for in this case aldehyde **I** isolated after the removal of the solvent contained the least amount of impurities, in contrast to the product extracted with ether. (2-Bornylidene)acetaldehyde of high purity was frozen out from the hexane solution. mp 46–50°C. IR spectrum, cm^{-1}: 2955, 2870 (C–H), 2745 ($CH_{aldehyde}$), 1680 o.s ($C{=}O_{conjug.aldehyde}$), 1640 s ($C{=}C_{conjug}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.77 s (3H, 1-CH_3), 0.95 s (3H, 7-CH_3-*anti*), 1.00 s (3H, 7-CH_3-*syn*), 1.22 m (2H, H^5-*endo* + H^6-*endo*), 1.70 t.d (1H, H^6-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{exo,endo}$ 4 Hz), 1.85 t.t.d (1H, H^5-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{exo,endo}$ = $^3J_{5\text{-}exo,4}$ = 4, $^4J_{3\text{-}exo,5\text{-}exo}$ 2.4 Hz), 2.09 t (1H, H^4, $^3J_{3\text{-}exo,4}$ = $^3J_{5\text{-}exo,4}$ = 4 Hz), 2.37 d.d (1H, H^3-*endo*, ^2J 18, $^4J_{3,11}$ 2.4 Hz), 2.86 d.d.t (1H, H^3-*exo*, ^2J 18, $^3J_{3\text{-}exo,4}$ 4, $^4J_{3,11}$ = $^4J_{3\text{-}exo,5\text{-}exo}$ = 2.4 Hz), 5.79 d.t (1H, H^{11}, $^3J_{11,12}$ 8, 2 $^4J_{3,11}$ 2.4 Hz), 9.84 d (1H, H^{12}, $^3J_{11,12}$ 8 Hz).

5-Aryl-4-methoxycarbonylcyclohexane-1,3-diones IIIe–IIIg were obtained by the known procedure [14] from dimethyl malonate and (β-aryl)vinyl methyl ketones (products of equimolar condensation of acetone with appropriate aromatic aldehydes). 4-Methoxycarbonyldimedone (**IIIg**) was analogously obtained from mesityl oxide and dimethyl malonate.

The three-component condensation was carried out by common procedure [12]. Equimolar amounts (2 mmol) of (2-isobornylidene)acetaldehyde (**I**), of 2-naphthylamine (**II**), and of an appropriate β-diketone in 10 ml of ethanol were boiled without catalyst till the completion of the reaction (3–4 h, GLC monitoring), then the reaction mixture was evaporated to ~1/4 of the initial volume, and the reaction product was precipitated by adding excess ether. The precipitated crystalline substance was filtered off and recrystallized. At crystallization from ethanol the precipitated compound is enriched with the (12*R*)-isomer prevailing in the reaction mixture [or with the mixture of (12*R*)-isomers when the reaction yields 4 stereoisomers]. The mixture of compounds obtained by evaporation of mother liquors where are dominanted the (12*S*)-isomers was crystallized from anhydrous acetone. Repeating many times the procedures of dissolution–crystallization we obtained samples enriched with the corresponding isomers up to 80% and more. The separation of stereoisomers with respect to atoms C^8 and/or C^9 was carried out by crystallization from a mixture ethanol–benzene (see below). The registering of the spectra was performed using the samples containing no less than 80% of the desired stereoisomer.

12-(2-Bornylidene)methyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones VIIa, VIIIa were obtained in an overall yield 60%. After 5 crystallizations from ethanol a sample was obtained containing ~ 85% of (12*R*)-isomer **VIIa**. The substance isolated from the mother liquor after 6 crystallizations from acetone contained ~ 82% of (12*S*)-isomer **VIIIa**.

(12*R*)-12-(2-Bornylidene)methyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIa). IR spectrum, cm^{-1}: 3425, 3260 (NH), 3075, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 ($C=C_{arom}$), 1190 (C–N–C), 810, 750 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.56 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.79 s (3H, 7-CH_3-*anti*), 0.86 d.d.d (1H, H$^{6'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.20 d.d.d (1H, H$^{5'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.42 d.t (1H, H$^{6'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.72 t.t.d (1H, H$^{5'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{5'\text{-}exo,4'} = 4$, $^WJ_{5'\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.79 t (1H, H$^{4'}$, $^3J_{4',5'\text{-}exo} = {}^3J_{4',3'\text{-}exo} =$ 4 Hz), 1.84 m (2H, C^9H_2), 1.91 d.d.d (1H, H$^{8a'}$, ^2J 16, $^3J_{a',a}$ 9, $^3J_{a',e}$ 5 Hz), 2.19 br.d (1H, H$^{3'}$-*endo*, ^2J 16, $^4J_{3',11'}$ 2 Hz), 2.21 d.t (1H, H$^{8e'}$, ^2J 16, $^3J_{e',a} = {}^3J_{e',e} = 5$ Hz), 2.23 d.d.d (1H, H$^{10a'}$, ^2J 18, $^3J_{a',a}$ 9, $^3J_{a',e}$ 5 Hz), 2.56 d.t (1H, H$^{10e'}$, ^2J 18, $^3J_{e',a} = {}^3J_{e',e} = 5$ Hz), 3.10 br.d.d (1H, H$^{3'}$-*exo*, ^2J 16, $^3J_{3'\text{-}exo,4}$ 4, $^WJ_{3'\text{-}exo,5'\text{-}exo} = {}^4J_{3',11'} = 2$ Hz), 4.80 br.d (1H, H^{11}, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.16 d (1H, H^{12}, ^3J 9.6 Hz), 7.18 d (1H, H^5, ^3J 9 Hz), 7.32 t and 7.49 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.71 d and 7.80 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.88 d (1H, H^6, ^3J 9 Hz), 9.48 s (1H, NH).

(12*S*)-12-(2-Bornylidene)methyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIIa). IR spectrum, cm^{-1}: 3420, 3180 (NH), 3070, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 ($C=C_{arom}$), 1190 (C–N–C), 810, 750 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.57 s (3H, 1-CH_3), 0.58 s (3H, 7-CH_3-*syn*), 0.79 c (3H, 7-CH_3-*anti*), 0.95 d.d.d (1H, H$^{6'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.07 d.d.d (1H, H$^{5'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.45 d.t (1H, H$^{6'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.70 m (3H, H$^{5'}$-*exo* + C^9H_2), 1.78 t (1H, H$^{4'}$, $^3J_{4',5'\text{-}exo} = {}^3J_{4',3'\text{-}exo} =$ 4 Hz), 1.96 d.d.d (1H, H$^{8a'}$, ^2J 16, $^3J_{a',a}$ 9, $^3J_{a',e}$ 5 Hz), 2.20 d (1H, H$^{8e'}$, ^2J 16, $^3J_{e',a} = {}^3J_{e',e} = 5$ Hz), 2.24 d.d.d (1H, H$^{10a'}$, ^2J 18, $^3J_{a',a}$ 9, $^3J_{a',e}$ 5 Hz), 2.54 br.d (1H, H$^{3'}$-*endo*, ^2J 16, $^4J_{3',11'}$ 2 Hz), 2.56 d.t (1H, H$^{10e'}$, ^2J 18, $^3J_{e',a} = {}^3J_{e',e} = 5$ Hz), 2.58 br.d.d (1H, H$^{3'}$-*exo*, ^2J 16, $^3J_{32\text{-}exo,4'}$ 4, $^WJ_{32\text{-}exo,5'\text{-}exo} = {}^4J_{3',11'} = 2$ Hz), 4.83 br.d (1H, H$^{11'}$, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.14 d (1H, H^{12}, ^3J 9.6 Hz), 7.19 d (1H, H^5, ^3J 9 Hz), 7.32 t and 7.44 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.71 d and 7.80 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.79 d (1H, H^6, ^3J 9 Hz), 9.50 s (1H, NH).

12-(2-Bornylidene)methyl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones VIIb, VIIIb were obtained in overall yield 68%. Samples containing ~85% of (12*R*)-isomer and ~83% of (12*S*)-isomer were obtained by procedures described above.

(12*R*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIb). IR spectrum, cm^{-1}: 3420, 3275 (NH), 3090, 3020 (CH_{arom}), 2955, 2925, 2870 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 ($C=C_{arom}$), 1150 (C–N–C), 810, 745 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.47 s (3H, 1-CH_3), 0.59 s (3H, 7-CH_3-*syn*), 0.74 s (3H, 7-CH_3-*anti*), 0.92 d.d.d (1H, H$^{6'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 0.98 s and 1.01 s (3 H each, two 9-CH_3), 1.12 d.d.d (1H, H$^{5'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.41 d.t (1H, H$^{6'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.68 t.t.d (1H, H$^{5'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{5'\text{-}exo,4'} = 4$, $^WJ_{5'\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.73 t (1H, H$^{4'}$, $^3J_{4',5'\text{-}exo} = {}^3J_{4',3'\text{-}exo} = 4$ Hz), 2.00 d (1H, H$^{8a'}$, ^2J 16 Hz), 2.12 br.d (1H, H$^{3'}$-*endo*, ^2J 16, $^4J_{3',11'}$ 2 Hz), 2.28 d (1H, H$^{8e'}$, ^2J 16 Hz), 2.30 d (1H,

$H^{10a'}$, ^2J 18 Hz), 2.45 d (1H, $H^{10e'}$, ^2J 18 Hz), 3.01 br.d.d (1H, $H^{3'}$-*exo*, ^2J 16, $^3J_{3'\text{-}exo,4'}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{3,11}$ = 2 Hz), 4.83 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{3,11}$ 2 Hz), 5.10 d (1H, H^{12}, ^3J 9.6 Hz), 7.17 d (1H, H^5, ^3J 9 Hz), 7.31 t and 7.47 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.68 d and 7.77 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.86 d (1H, H^6, ^3J 9 Hz), 9.50 s (1H, NH).

(12*S*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIIb). IR spectrum, cm^{-1}: 3420, 3190 (NH), 3080, 3020 (CH_{arom}), 2955, 2925, 2870 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 ($C{=}C_{arom}$), 1150 (C–N–C), 810, 745 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.51 s (6H, 1-CH_3 + 7-CH_3-*syn*), 0.74 s (3H, 7-CH_3-*anti*), 0.96 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 0.99 d.d.d (1H, H^{52}-*endo* , ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.00 s and 1.01 s (3 H each, two 9-CH_3), 1.47 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.65 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.77 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.05 d (1H, H^{8a2}, ^2J 16 Hz), 2.28 d (1H, H^{8e2}, ^2J 16 Hz), 2.33 d (1H, H^{10a2}, ^2J 18 Hz), 2.45 d (1H, H^{10e2}, ^2J 18 Hz), 2.61 br.d.d (1H, H^{32}-*exo*, ^2J 16, $^3J_{3'\text{-}exo,4'}$ 4, $^WJ_{32\text{-}exo,5'\text{-}exo} = {}^4J_{3',11'}$ = 2 Hz), 2.66 br.d (1H, H^{32}-*endo*, ^2J 16, $^4J_{3',11'}$ 2 Hz), 4.79 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.11 d (1H, H^{12}, ^3J 9.6 Hz), 7.18 d (1H, H^5, ^3J 9 Hz), 7.30 t and 7.43 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.68 d and 7.74 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.84 d (1H, H^6, ^3J 9 Hz), 9.50 s (1H, NH).

12-(2-Bornylidene)methyl-9-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones VIIc, VIId, VIIIc, VIIId were obtained in overall yield 64%. After 6 crystallization of the stereoisomers mixture from ethanol a sample was obtained containing ~ 90% of a mixture of (12*R*)-isomers **VIIc** and **VIId**. A mixture containing ~ 87% of (12*S*)-isomers **VIIIc** and **VIIId** was obtained by 7 crystallizations from acetone of the compound isolated from the mother liquor. The separation of *cis*- and *trans*-isomers was performed by multiple crystallization from the mixture ethanol–benzene, 1:2. The spectra were registered from the samples containing no less than 80% of an individual stereoisomer.

(9*R*,12*R*)-12-(2-Bornylidene)methyl-9-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIc). IR spectrum, cm^{-1}: 3425, 3265 (NH), 3085, 3025 (CH_{arom}), 2950, 2930, 2865 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 ($C{=}C_{arom}$), 1145 (C–N–C), 810, 745, 700 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.56 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.95 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.20 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.43 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.72 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{5'\text{-}exo,4'}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.80 t (1H, H^{42}, $^3J_{42,5'\text{-}exo} = {}^3J_{42,3'\text{-}exo}$ = 4 Hz), 2.22 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{3',11'}$ 2 Hz), 2.60 d.d (1H, H^8, ^2J 16, ^3J 6 Hz), 2.72 d.d (1H, H^8, ^2J 16, ^3J 6 Hz), 2.80 d.d (1H, H^{10}, ^2J 18, ^3J 6 Hz), 2.90 d.d (1H, H^{10}, ^2J 18, ^3J 6 Hz), 3.20 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{3'\text{-}exo,4'}$ 4, $^WJ_{32\text{-}exo,5'\text{-}exo} = {}^4J_{3',11'}$ = 2 Hz), 3.47 m (1H, H^9, 4 ^3J 6 Hz), 4.71 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.15 d (1H, H^{12}, ^3J 9.6 Hz), 7.16 d (1H, H^5, ^3J 9 Hz), 7.34 m (5H, Ph), 7.39 t and 7.49 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.70 d and 7.79 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.89 d (1H, H^6, ^3J 9 Hz), 9.48 s (1H, NH).

(9*S*,12*S*)-12-(2-Bornylidene)methyl-9-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIIc). IR spectrum, cm^{-1}: 3430, 3175 (NH), 3088, 3025 (CH_{arom}), 2950, 2925, 2865 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 ($C{=}C_{arom}$), 1145 (C–N–C), 810, 745, 700 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.57 s (3H, 1-CH_3), 0.61s (3H, 7-CH_3-*syn*), 0.79 s (3H, 7-CH_3-*anti*), 0.94 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.06 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.49 d.t (1H, H^{62}-*exo* , $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.68 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.81 t (1H, H^{42}, $^3J_{4',52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.34 d.d (1H, H^8, ^2J 16, ^3J 6 Hz), 2.60 br.d (1H, H^{32}-*endo*, ^2J 16, $^4J_{3',11'}$ 2 Hz), 2.66 d.d (1H, H^8, ^2J 16, ^3J 6 Hz), 2.71 br.d.d (1H, H^{32}-*exo*, ^2J 16, $^3J_{32\text{-}exo,4'}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{3',11'}$ = 2 Hz), 2.81 d.d (1H, H^{10}, ^2J 18, ^3J 6 Hz), 2.95 d.d (1H, H^{10}, ^2J 18, ^3J 6 Hz), 3.47 m (1H, H^9, 4 ^3J 6 Hz), 4.72 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.16 d (1H, H^{12}, ^3J 9.6 Hz), 7.22 d (1H, H^5, ^3J 9 Hz), 7.30 m (5H, Ph), 7.41 t and 7.46 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.70 d and 7.80 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.90 d (1H, H^6, ^3J 9 Hz), 9.52 s (1H, NH).

(9*S*,12*R*)-12-(2-Bornylidene)methyl-9-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIId). IR spectrum, cm^{-1}: 3425, 3265 (NH), 3085, 3025 (CH_{arom}), 2950, 2930, 2865 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 ($C{=}C_{arom}$), 1145 (C–N–C), 810, 745, 700 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.62 s (3H, 1-CH_3), 0.67 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.92 d.d.d

(1H, H$^{6'}$-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.22 d.d.d (1H, H$^{5'}$-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.45 d.t (1H, H^{62}-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo}$ 4 Hz), 1.71 t.t.d (1H, H$^{5'}$-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo} = {}^{3}J_{5'\text{-}exo,4'} = 4$, $^{W}J_{5'\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.81 t (1H, H$^{4'}$, $^{3}J_{4',5'\text{-}exo} = {}^{3}J_{4',32\text{-}exo} = 4$ Hz), 2.24 br.d (1H, H^{32}-*endo*, ^{2}J 16.4, $^{4}J_{3',11'}$ 2 Hz), 2.56 d.d (1H, H^{10a2}, ^{2}J 18, $^{3}J_{a,a2}$ 9 Hz), 2.58 d.d (1H, H^{8a2}, ^{2}J 16, $^{3}J_{a,a2}$ 9 Hz), 2.76 d.d (1H, H^{8e2}, ^{2}J 16, $^{3}J_{a,e2}$ 4 Hz), 2.92 d.d (1H, H^{10e2}, ^{2}J 18, $^{3}J_{a,e2}$ 4 Hz), 3.14 br.d.d (1H, H^{32}-*exo*, ^{2}J 16.4, $^{3}J_{32\text{-}exo,4'}$ 4, $^{W}J_{32\text{-}exo,52\text{-}exo} = {}^{4}J_{3',112} = 2$ Hz), 3.92 t.t (1H, H^{9a}, 2 $^{3}J_{a,a2}$ 9, 2 $^{3}J_{a,e2}$ 4 Hz), 4.87 br.d (1H, H^{112}, ^{3}J 9.6, 2 $^{4}J_{32,112}$ 2 Hz), 5.16 d (1H, H^{12}, ^{3}J 9.6 Hz), 7.19 d (1H, H^{5}, ^{3}J 9 Hz), 7.34 m (5H, Ph), 7.39 t and 7.51 t (1H each, H^{2} and H^{3}, ^{3}J 7 Hz), 7.70 d and 7.79 d (1H each, H^{1} and H^{4}, ^{3}J 7 Hz), 7.93 d (1H, H^{6}, ^{3}J 9 Hz), 9.58 s (1H, NH).

(9*R*,12*S*)-12-(2-Bornylidene)methyl-9-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (VIIId). IR spectrum, cm^{-1}: 3430, 3175 (NH), 3088, 3025 (CH_{arom}), 2950, 2925, 2865 (CH_{aliph}), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 (C=C_{arom}), 1145 (C–N–C), 810, 745, 700 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.58 s (3H, 1-CH_3), 0.65 s (3H, 7-CH_3-*syn*), 0.75 s (3H, 7-CH_3-*anti*), 1.00 d.d.d (1H, H^{62}-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.08 d.d.d (1H, H^{52}-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.52 d.t (1H, H^{62}-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo}$ 4 Hz), 1.67 t.t.d (1H, H^{52}-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo} = {}^{3}J_{52\text{-}exo,42} = 4$, $^{W}J_{52\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.80 t (1H, H^{42}, $^{3}J_{42,52\text{-}exo} = {}^{3}J_{42,32\text{-}exo} = 4$ Hz), 2.42 d.d (1H, H^{8a2}, ^{2}J 16, $^{3}J_{a,a'}$ 9 Hz), 2.60 br.d (1H, H^{32}-*endo*, ^{2}J 16, $^{4}J_{32,112}$ 2 Hz), 2.65 br.d.d (1H, H^{32}-*exo*, ^{2}J 16, $^{3}J_{32\text{-}exo,42}$ 4, $^{W}J_{32\text{-}exo,52\text{-}exo} = {}^{4}J_{32,112} = 2$ Hz), 2.72 d.d (1H, H^{10a2}, ^{2}J 18, $^{3}J_{a,a2}$ 9 Hz), 2.78 d.d (1H, H^{8e2}, ^{2}J 16, $^{3}J_{a,e2}$ 4 Hz), 2.94 d.d (1H, H^{10e2}, ^{2}J 18, $^{3}J_{a,e2}$ 4 Hz), 3.64 t.t (1H, H^{9a}, 2 $^{3}J_{a,a2}$ 9, 2 $^{3}J_{a,e2}$ 4 Hz), 4.82 br.d (1H, H^{112}, ^{3}J 9.6, 2 $^{4}J_{32,112}$ 2 Hz), 5.20 d (1H, H^{12}, ^{3}J 9.6 Hz), 7.22 d (1H, H^{5}, ^{3}J 9 Hz), 7.30 m (5H, Ph), 7.40 t and 7.46 t (1H each, H^{2} and H^{3}, ^{3}J 7 Hz), 7.72 d and 7.89 d (1H each, H^{1} and H^{4}, ^{3}J 7 Hz), 7.77 d (1H, H^{6}, ^{3}J 9 Hz), 9.61 s (1H, NH).

13-(2-Bornylidene)methyl-7,13-dihydro-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-ones IX and X were obtained in overall yield 44%. After 4 crystallizations from ethanol the sample obtained contained ~82% of (12*R*)-isomer. The substance isolated from the mother liquor after 5 crystallizations from acetone contained ~ 84% of (12*S*)-isomer.

(13*R*)-13-(2-Bornylidene)methyl-7,13-dihydro-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-one (IX). IR spectrum, cm^{-1}: 3460, 3280 (NH), 3060, 3025 (CH_{arom}), 2955, 2925, 2870 (CH_{aliph}), 1590, 1560 (HN–C=C–C=O, "vinilog of amide"), 1505 (C=C_{arom}), 1160 (C–N–C), 770, 730 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.36 s (3H, 1-CH_3), 0.61 s (3H, 7-CH_3-*syn*), 0.68 s(3H, 7-CH_3-*anti*), 0.95 d.d.d (1H, H^{62}-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.20 d.d.d (1H, H$^{5'}$-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.33 d.t (1H, H$^{6'}$-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo}$ 4 Hz), 1.56 t.t.d (1H, H$^{5'}$-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo} = {}^{3}J_{5'\text{-}exo,4'} = 4$, $^{W}J_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.69 t (1H, H^{42}, $^{3}J_{42,52\text{-}exo} = {}^{3}J_{4',32\text{-}exo} = 4$ Hz), 2.26 br.d (1H, H^{32}-*endo*, ^{2}J 16, $^{4}J_{32,112}$ 2 Hz), 3.24 br.d.d (1H, H^{32}-*exo*, ^{2}J 16, $^{3}J_{32\text{-}exo,42}$ 4, $^{W}J_{32\text{-}exo,52\text{-}exo} = {}^{4}J_{32,112} = 2$ Hz), 4.22 br.d (1H, H^{112}, ^{3}J 9.6, 2 $^{4}J_{3',11'}$ 2 Hz), 4.70 d (1H, H^{12}, ^{3}J 9.6 Hz), 7.10 d (1H, H^{5}, ^{3}J 9 Hz), 7.50 m (4H), 7.80 m (5H), 8.80 d (1H, H^{8}, ^{3}J 8 Hz), 10.45 s (1H, NH).

(13*S*)-13-(2-Bornylidene)methyl-7,13-dihydro-12*H*-benzo[*f*]indeno[1,2-*b*]quinolin-12-one (X). IR spectrum, cm^{-1}: 3460, 3170 (NH), 3060, 3025 (CH_{arom}), 2955, 2925, 2870 (CH_{aliph}), 1590, 1560 (HN–C=C–C=O, "vinilog of amide"), 1505 (C=C_{arom}), 1160 (C–N–C), 770, 735 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.34 s (3H, 1-CH_3), 0.61 s (3H, 7-CH_3-*syn*), 0.68 s (3H, 7-CH_3-*anti*), 0.97 d.d.d (1H, H^{62}-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.10 d.d.d (1H, H^{52}-*endo*, ^{2}J 12, $^{3}J_{endo,endo}$ 8, $^{3}J_{endo,exo}$ 4 Hz), 1.35 d.t (1H, H^{62}-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo}$ 4 Hz), 1.59 t.t.d (1H, H^{52}-*exo*, $^{2}J = {}^{3}J_{exo,exo} = 12$, $^{3}J_{endo,exo} = {}^{3}J_{52\text{-}exo,42} = 4$, $^{W}J_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.71 t (1H, H^{42}, $^{3}J_{42,52\text{-}exo} = {}^{3}J_{42,32\text{-}exo} = 4$ Hz), 2.56 br.d (1H, H^{32}-*endo*, ^{2}J 16, $^{4}J_{32,112}$ 2 Hz), 2.68 br.d.d (1H, H^{32}-*exo*, ^{2}J 16, $^{3}J_{32\text{-}exo,42}$ 4, $^{W}J_{32\text{-}exo,52\text{-}exo} = {}^{4}J_{32,112} = 2$ Hz), 4.20 br.d (1H, H^{112}, ^{3}J 9.6, 2 $^{4}J_{32,112}$ 2 Hz), 4.70 d (1H, H^{12}, ^{3}J 9.6 Hz), 7.12 d (1H, H^{5}, ^{3}J 9 Hz), 7.50 m (4H), 7.80 m (5H), 8.76 d (1H, H^{8}, ^{3}J 8 Hz), 10.47 s (1H, NH).

12-(2-Bornylidene)methyl-9,9-dimethyl-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo-[*a*]acridin-11-ones XId–XIVd were obtained in overall yield 65%. The samples enriched to 80% and more with each of the four stereoisomers were obtained by the procedure described above for phendione derivatives.

(8*S*,12*R*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo-[*a*]acridin-11-one (XId). IR spectrum, cm^{-1}: 3310, 3200 (NH), 3085, 3070, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1730 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 (C=C_{arom}), 1240, 1185 (C–O–C), 1150 (C–N–C), 815, 750 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.52 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.78 s (3H,

7-CH_3-*anti*), 0.85 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.05 and 1.10 s (3 H each, two 9-CH_3), 1.15 d.d.d (1H, H^{52} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.44 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.70 t.t.d (1H, H^{52} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.75 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.14 br.d (1H, H^{32} -*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.31 d (1H, H^{10}-*cis*, ^2J 18 Hz), 2.78 d (1H, H^{10}-*trans*, ^2J 18 Hz), 3.00 br.d.d (1H, H^{32} -*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112}$ = 2 Hz), 3.04 s (1H, H^8), 3.57 s (3H, $COOCH_3$), 4.87 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.08 d (1H, H^{12}, ^3J 9.6 Hz), 7.18 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.50 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.72 d and 7.80 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.87 d (1H, H^6, ^3J 9 Hz), 9.72 s (1H, NH).

(8*R*,12*S*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo-[*a*]acridin-11-one (XIId). IR spectrum, cm^{-1}: 3310, 3200 (NH), 3085, 3070, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1730 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 (C=C_{arom}), 1240, 1185 (C–O–C), 1150 (C–N–C), 815, 750 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.58 s (3H, 1-CH_3), 0.59 s (3H, 7-CH_3-*syn*), 0.79 s (3H, 7-CH_3-*anti*), 0.94 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.04 d.d.d (1H, H^{52} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.05 and 1.08 s (3 H each, two 9-CH_3), 1.50 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.68 t.t.d (1H, H^{52} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.80 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.32 d (1H, H^{10}-*cis*, ^2J 18 Hz), 2.52 br.d (1H, H^{32} -*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.65 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112}$ = 2 Hz), 2.78 d (1H, H^{10}-*trans*, ^2J 18 Hz), 3.09 s (1H, H^8), 3.57 s (3H, $COOCH_3$), 4.82 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.08 d (1H, H^{12}, ^3J 9.6 Hz), 7.19 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.45 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.72 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.80 d (1H, H^6, ^3J 9 Hz), 9.72 s (1H, NH).

(8*R*,12*R*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIId). IR spectrum, cm^{-1}: 3330, 3200 (NH), 3085, 3075, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1730 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 (C=C_{arom}), 1240, 1185 (C–O–C), 1150 (C–N–C), 815, 750 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.50 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.78 s (3H, 7-CH_3-*anti*), 0.85 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.06 and 1.10 s (3 H each, two 9-CH_3), 1.13 d.d.d (1H, H^{52} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.44 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.72 t.t.d (1H, H^{52} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.74 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.12 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.46 d (1H, H^{10}-*trans*, ^2J 18 Hz), 2.64 d (1H, H^{10}-*cis*, ^2J 18 Hz), 2.99 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112}$ = 2 Hz), 3.29 s (1H, H^8), 3.58 s (3H, $COOCH_3$), 4.87 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.08 d (1H, H^{12}, ^3J 9.6 Hz), 7.18 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.49 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.72 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.87 d (1H, H^6, ^3J 9 Hz), 9.63 c (1H, NH).

(8*S*,12*S*)-12-(2-Bornylidene)methyl-9,9-dimethyl-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIVd). IR spectrum, cm^{-1}: 3315, 3190 (NH), 3085, 3075, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1730 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1495 (C=C_{arom}), 1240, 1185 (C–O–C), 1150 (C–N–C), 815, 750 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.58 s (6H, 1-CH_3 + 7-CH_3-*syn*), 0.78 s (3H, 7-CH_3-*anti*), 0.96 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.06 d.d.d (1H, H^{52} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.07 and 1.14 s (3 H each, two 9-CH_3), 1.50 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.69 t.t.d (1H, H^{52} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.77 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.43 d (1H, H^{10}-*trans*, ^2J 18 Hz), 2.48 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.54 br.d.d (1H, H^{32} -*exo*, ^2J 16.4, $^3J_{3'\text{-}exo,42}$ = 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112}$ = 2 Hz), 2.66 d (1H, H^{10}-*cis*, ^2J 18 Hz), 3.31 s (1H, H^8), 3.62 s (3H, $COOCH_3$), 4.82 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.09 d (1H, H^{12}, ^3J 9.6 Hz), 7.19 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.44 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.72 d and 7.80 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.82 d (1H, H^6, ^3J 9 Hz), 9.67 s (1H, NH).

12-(2-Bornylidene)methyl-8-methoxycarbonyl-9-(2,4,6-trimethylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones XIe–XIVe were obtained in overall yield 62%. The samples enriched to 80% and more with each of the four stereoisomers were obtained by the procedure described above for phendione derivatives.

(8*S*,9*R*,12*R*)-12-(2-Bornylidene)methyl-8-methoxycarbonyl-9-(2,4,6-trimethylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIe). IR spectrum, cm^{-1}: 3410, 3280 (NH), 3085, 3060,

3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1490 ($C=C_{arom}$), 1255 (C–O–C), 1145 (C–N–C), 815, 760 ($C–H_{arom}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.60 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.92 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.20 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.45 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.65 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42} = 4$, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.81 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo} = 4$ Hz), 2.20 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.26 s (3H) and 2.39 s (6H) (CH_{3arom}), 2.50 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz,), 3.07 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112} = 2$ Hz,), 3.30 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.34d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz,), 3.39 c (3H, $COOCH_3$), 4.24 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.88 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.15 d (1H, H^{12}, ^3J 9.6 Hz), 6.82 s (2H, H_{arom}), 7.20 d (1H, H^5, ^3J 9 Hz), 7.36 t and 7.48 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.73 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.78 d (1H, H^6, ^3J 9 Hz), 9.66 s (1H, NH).

(8*R*,9*S*,12*S*)-12-(2-Bornylidene)methyl-8-methoxycarbonyl-9-(2,4,6-trimethylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIe). IR spectrum, cm^{-1}: 3400, 3190 (NH), 3085, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1490 ($C=C_{arom}$), 1255 (C–O–C), 1145 (C–N–C), 815, 755 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.60 s (3H, 1-CH_3), 0.66 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.92 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.07 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.50 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.73 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42} = 4$, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.81 t (1H, H^{42}, $^3J_{42\,52\text{-}exo} = {}^3J_{42,32\text{-}exo} = 4$ Hz), 2.26 s (3H) and 2.39 s (6H) ($CH_{3\ arom}$), 2.50 m (2H, H^{32}-*endo* + H^{32}-*exo*), 2.63 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.22 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.32 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.38 c (3H, $COOCH_3$), 4.27 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.93 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.14 d (1H, H^{12}, ^3J 9.6 Hz), 6.82 s (2H_{arom}), 7.19 d (1H, H^5, ^3J 9 Hz), 7.36 t and 7.50 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.73 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.89 d (1H, H^6, ^3J 9 Hz), 9.63 s (1H, NH).

(8*R*,9*S*,12*R*)-12-(2-Bornylidene)methyl-8-methoxycarbonyl-9-(2,4,6-trimethylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIIe). IR spectrum, cm^{-1}: 3400, 3270 (NH), 3085, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1490 ($C=C_{arom}$), 1250 (C–O–C), 1150 (C–N–C), 815, 750 ($C–H_{arom}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.58 s (3H, 1-CH_3), 0.60 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.91 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.18 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.45 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.66 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,4''} = 4$, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.76 t (1H, H^{42}, $^3J_{42,52\text{-}exo} = {}^3J_{42,32\text{-}exo} = 4$ Hz), 2.19 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.26 s (3H) and 2.39 s (6H) (CH_{3arom}), 2.66 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.08 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112} = 2$ Hz), 3.18 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.38 c (3H, $COOCH_3$), 3.63 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 4.05 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.99 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.20 d (1H, H^{12}, ^3J 9.6 Hz), 6.82 s (2H_{arom}), 7.20 d (1H, H^5, ^3J 9 Hz), 7.36 t and 7.46 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.73 d and 7.82 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.79 d (1H, H^6, ^3J 9 Hz), 9.76 s (1H, NH).

(8*S*,9*R*,12*S*)-12-(2-Bornylidene)methyl-8-methoxycarbonyl-9-(2,4,6-trimethylphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIVe). IR spectrum, cm^{-1}: 3400, 3180 (NH), 3085, 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1600, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1490 ($C=C_{arom}$), 1260 (C–O–C), 1150 (C–N–C), 815, 750 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.58 s (3H, 1-CH_3), 0.66 s (3H, 7-CH_3-*syn*), 0.80 s (3H, 7-CH_3-*anti*), 0.94 d.d.d (1H, $H^{6'}$-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.12 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.48 d.t (1H, $H^{6'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.72 t.t.d (1H, $H^{5'}$-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{5'\text{-}exo,4'} = 4$, $^WJ_{5'\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.76 t (1H, $H^{4'}$, $^3J_{4',5'\text{-}exo} = {}^3J_{4',3'\text{-}exo} = 4$ Hz), 2.26 s (3H) and 2.39 s (6H) (CH_{3arom}), 2.56 m (2H, $H^{3'}$-*endo* + H3'-*exo*), 2.62 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.23 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.38 c (3H, $COOCH_3$), 3.64 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 4.04 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 5.07 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.20 d (1H, H^{12}, ^3J 9.6 Hz), 6.82 s (2H_{arom}), 7.19 d (1H, H^5, ^3J 9 Hz), 7.36 t and 7.51 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.73 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.94 d (1H, H^6, ^3J 9 Hz), 9.74 s (1H, NH).

12-(2-Bornylidene)methyl-9-(3,4-dimethoxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-

7*H*-benzo[*a*]acridin-11-ones XIf–XIVf were obtained in overall yield 59%. The samples enriched to 80% and more with each of the four stereoisomers were obtained by the procedure described above for phendione derivatives.

(8*S*,9*R*,12*R*)-12-(2-Bornylidene)methyl-9-(3,4-dimethoxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIf). IR spectrum, cm^{-1}: 3420, 3275 (NH), 3065, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1265, 1245 (C–O–C), 1145 (C–N–C), 810, 755 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.61 s (3H, 1-CH_3), 0.69 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.93 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.15 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.45 d.t (1H, H^{62}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.62 t.t.d (1H, H^{52}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.84 t (1H, H^{42}, $^3J_{42,52\text{-}exo}$ = $^3J_{42,32\text{-}exo}$ = 4 Hz), 2.20 br.d (1H, H^{32}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.70 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 2.95 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo}$ = $^4J_{32,112}$ = 2 Hz), 3.29 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.32 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.50 s (3H, $COOCH_3$), 3.79 s (6H, 2$OCH_{3\ arom}$), 4.19 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.85 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.19 d (1H, H^{12}, ^3J 9.6 Hz), 6.81 d (2H_{arom}) and 6.96 s (1H_{arom}), 7.19 d (1H, H^5, ^3J 9 Hz), 7.35 t and 7.49 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.70 d and 7.82 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.90 d (1H, H^6, ^3J 9 Hz), 9.55 s (1H, NH).

(8*R*,9*S*,12*S*)-12-(2-Bornylidene)methyl-9-(3,4-dimethoxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIf). IR spectrum, cm^{-1}: 3420, 3330 (NH), 3065, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1265, 1245 (C–O–C), 1145 (C–N–C), 810, 755 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.60 s (3H, 1-CH_3), 0.63 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.96 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.11 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.47 d.t (1H, H^{62}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = 4 Hz), 1.65 t.t.d (1H, H^{52}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ = 2 Hz), 1.81 t (1H, H^{42}, $^3J_{42,52\text{-}exo}$ = $^3J_{42,32\text{-}exo}$ = 4 Hz), 2.68 m (2H, H^{32}-*endo* + H^{32}-*exo*), 2.83 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.32 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.34 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.50 s (3H, $COOCH_3$), 3.81 s (6H, 2OCH_{3arom}), 4.21t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.94 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.12 d (1H, H^{12}, ^3J 9.6 Hz), 6.81 s (2H_{arom}) and 6.96 s (1H_{arom}), 7.17 d (1H, H^5, ^3J 9 Hz), 7.35 t and 7.48 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.70 d and 7.78 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.89 d (1H, H^6, ^3J 9 Hz), 9.56 s (1H, NH).

(8*R*,9*S*,12*R*)-12-(2-Bornylidene)methyl-9-(3,4-dimethoxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIIf). IR spectrum, cm^{-1}: 3420, 3275 (NH), 3065, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1265, 1245 (C–O–C), 1145 (C–N–C), 810, 755 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.61 s (3H, 1-CH_3), 0.68 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.95 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.17 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.47 d.t (1H, H^{62}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.63 t.t.d (1H, H^{52}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ = 2 Hz), 1.81 t (1H, H^{42}, $^3J_{42,52\text{-}exo}$ = $^3J_{42,32\text{-}exo}$ = 4 Hz), 2.19 br.d (1H, 3^{62}-*endo*, ^2J 16.4, $^4J_{32,112}$ 2 Hz), 2.78 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 2.98 br.d.d (1H, H^{32}-*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo}$ = $^4J_{32,112}$ = 2 Hz), 3.27 d.d (1H, H$^{10\varepsilon2}$, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.50 s (3H, $COOCH_3$), 3.62 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.79 s (6H, 2$OCH_{3\ arom}$), 3.99 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.87 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{32,112}$ 2 Hz), 5.20 d (1H, H^{12}, ^3J 9.6 Hz), 6.81 d (2H_{arom}) and 6.96 s (1H_{arom}), 7.18 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.48 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.70 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.88 d (1H, H^6, ^3J 9 Hz), 9.60 s (1H, NH).

(8*S*,9*R*,12*S*)-12-(2-Bornylidene)methyl-9-(3,4-dimethoxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIVf). IR spectrum, cm^{-1}: 3420, 3300 (NH), 3065, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1580 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1265, 1245 (C–O–C), 1145 (C–N–C), 810, 755 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.61 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.93 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.09 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.46 d.t (1H, H^{62}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.67 t.t.d (1H, H^{52}-*exo*, ^2J = $^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ = $^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ = 2 Hz), 1.79 t (1H, H^{42}, $^3J_{42,52\text{-}exo}$ = $^3J_{42,32\text{-}exo}$ = 4 Hz), 2.66 m (2H, H^{32}-*endo* + H^{32}-*exo*), 2.81 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.31 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.50 s

(3H, $COOCH_3$), 3.59 d (1H, H^{8a2} -*endo*, $^3J_{a,a2}$ 9 Hz), 3.81 s (6H, 2 $OCH_{3\ arom}$), 4.01 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.84 br.d (1H, $H^{11\,2}$, ^3J 9.6, 2 $^4J_{32\,,11\,2}$ 2 Hz), 5.12 d (1H, H^{12}, ^3J 9.6 Hz), 6.82 s (2H_{arom}), 6.96 s (1H_{arom}), 7.18 d (1H, H^5, ^3J 9 Hz), 7.33 t and 7.48 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.71 d and 7.78 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.88 d (1H, H^6, ^3J 9 Hz), 9.58 s (1H, NH).

12-(2-Bornylidene)methyl-9-(3,4-methylenedioxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-ones XIg–XIVg were obtained in overall yield 49%. The samples enriched to 80% and more with each of the four stereoisomers were obtained by the procedure described above for phendione derivatives.

(8*S*,9*R*,12*R*)-12-(2-Bornylidene)methyl-9-(3,4-methylenedioxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIg). IR spectrum, cm^{-1}: 3290, 3190 (NH), 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1575 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1250, 1230 (C–O–C), 1155 (C–N–C), 810, 800, 745 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.63 s (3H, 1-CH_3), 0.70 s (3H, 7-CH_3-*syn*), 0.85 s (3H, 7-CH_3-*anti*), 0.97 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.19 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.48 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.69 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.84 t (1H, H^{42}, $^3J_{42,52\ \text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.17 br.d (1H, H^{32} -*endo*, ^2J 16.4, $^4J_{32\,,11\,2}$ 2 Hz), 2.79 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 2.99 br.d.d (1H, H^{32} -*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32\,,11\,2}$ = 2 Hz), 3.32 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.35 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.56 s (3H, $COOCH_3$), 4.24 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.84 br.d (1H, $H^{11\,2}$, ^3J 9.6, 2 $^4J_{32\,,11\,2}$ 2 Hz), 5.18 d (1H, H^{12}, ^3J 9.6 Hz), 5.98 s (2H, OCH_2O), 6.76 m (2H_{arom}), 6.90 s (1H_{arom}), 7.16 d (1H, H^5, ^3J 9 Hz), 7.32 t and 7.45 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.69 d and 7.81 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.88 d (1H, H^6, ^3J 9 Hz), 9.65 s (1H, NH).

(8*R*,9*S*,12*S*)-12-(2-Bornylidene)methyl-9-(3,4-methylenedioxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIg). IR spectrum, cm^{-1}: 3290, 3190 (NH), 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1575 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1250, 1230 (C–O–C), 1155 (C–N–C), 810, 800, 745 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.65 s (3H, 1-CH_3), 0.67 s (3H, 7-CH_3-*syn*), 0.85 s (3H, 7-CH_3-*anti*), 0.98 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.21 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.44 d.t (1H, H^{62} -*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.63 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\ \text{-}exo,42}$ = 4, $^WJ_{52\ \text{-}exo,62\ \text{-}exo}$ 2 Hz), 1.80 t (1H, H^{42}, $^3J_{42\,,52\ \text{-}exo} = {}^3J_{42\,,32\ \text{-}exo}$ = 4 Hz), 2.69 m (2H, H^{32} -*endo* + H^{32} -*endo*), 2.82 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a2}$ 9 Hz), 3.30 d.d (1H, $H^{10\varepsilon2}$, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.32 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.56 s (3H, $COOCH_3$), 4.25 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.84 br.d (1H, $H^{11\,2}$, ^3J 9.6, 2 $^4J_{32\,,11\,2}$ 2 Hz), 5.12 d (1H, H^{12}, ^3J 9.6 Hz), 5.97 s (2H, OCH_2O), 6.75 m (2H_{arom}), 6.92 s (1H_{arom}), 7.16 d (1H, H^5, ^3J 9 Hz), 7.32 t and 7.45 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.68 d and 7.76 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.85 d (1H, H^6, ^3J 9 Hz), 9.66 s (1H, NH).

(8*R*,9*S*,12*R*)-12-(2-Bornylidene)methyl-9-(3,4-methylenedioxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIIIg). IR spectrum, cm^{-1}: 3290, 3170 (NH), 3060, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1575 (HN–C=C–C=O, "vinilog of amide"), 1520, 1500 (C=C_{arom}), 1250, 1230 (C–O–C), 1150 (C–N–C), 810, 800, 740 (CH_{arom}). ^1H NMR spectrum (DMSO-d_6) , δ, ppm: 0.62 s (3H, 1-CH_3), 0.68 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.99 d.d.d (1H, H^{62} -*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.18 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.47 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo}$ 4 Hz), 1.65 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo}$ = 12, $^3J_{endo,exo} = {}^3J_{52\ \text{-}exo,42}$ = 4, $^WJ_{52\text{-}exo,62\text{-}exo}$ 2 Hz), 1.85 t (1H, H^{42}, $^3J_{42,52\ \text{-}exo} = {}^3J_{42,32\text{-}exo}$ = 4 Hz), 2.18 br.d (1H, H^{32} -*endo*, ^2J 16.4, $^4J_{32\,,11\,2}$ 2 Hz), 2.79 d.d (1H, H^{10a2} -*exo*, ^2J 18, $^3J_{a,a2}$ 9 Hz), 2.96 br.d.d (1H, H^{32} -*exo*, ^2J 16.4, $^3J_{32\text{-}exo,42}$ 4, $^WJ_{32\text{-}exo,52\text{-}exo} = {}^4J_{32,112}$ = 2 Hz), 3.28 d.d (1H, $H^{10\varepsilon2}$, ^2J 18, $^3J_{a,e2}$ 4 Hz), 3.55 s (3H, $COOCH_3$), 3.63 d (1H, H^{8a2}, $^3J_{a,a2}$ 9 Hz), 3.96 t.d (1H, H^{9a}, 2 $^3J_{a,a2}$ 9, $^3J_{a,e2}$ 4 Hz), 4.85 br.d (1H, $H^{11\,2}$, ^3J 9.6, 2 $^4J_{32\,,11\,2}$ 2 Hz), 5.18 d (1H, H^{12}, ^3J 9.6 Hz), 5.98 s (2H, OCH_2O), 6.76 m (2H_{arom}), 6.91 s (1H_{arom}), 7.15 d (1H, H^5, ^3J 9 Hz), 7.31 t and 7.46 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.67 d and 7.76 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.84 d (1H, H^6, ^3J 9 Hz), 9.60 c (1H, NH).

(8*S*,9*R*,12*S*)-12-(2-Bornylidene)methyl-9-(3,4-methylenedioxyphenyl)-8-methoxycarbonyl-8,9,10,12-tetrahydro-7*H*-benzo[*a*]acridin-11-one (XIVg). IR spectrum, cm^{-1}: 3300, 3180 (NH), 3065, 3020 (CH_{arom}), 2950, 2930, 2870 (CH_{aliph}), 1740 (C=O, ester), 1595, 1575 (HN–C=C–C=O, "vinilog of amide"), 1520,

1500 (C=C_{arom}), 1250, 1230 (C–O–C), 1150 (C–N–C), 810, 800, 745 (CH_{arom}). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.61 s (3H, 1-CH_3), 0.62 s (3H, 7-CH_3-*syn*), 0.83 s (3H, 7-CH_3-*anti*), 0.99 d.d.d (1H, H^{62}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.21 d.d.d (1H, H^{52}-*endo*, ^2J 12, $^3J_{endo,endo}$ 8, $^3J_{endo,exo}$ 4 Hz), 1.43 d.t (1H, H^{62}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo}$ 4 Hz), 1.62 t.t.d (1H, H^{52}-*exo*, $^2J = {}^3J_{exo,exo} = 12$, $^3J_{endo,exo} = {}^3J_{5'\text{-}exo,4'} = 4$, $^WJ_{5'\text{-}exo,6'\text{-}exo}$ 2 Hz), 1.80 t (1H, H^{42}, $^3J_{4',5'\text{-}exo} = {}^3J_{4',3'\text{-}exo} =$ 4 Hz), 2.65 m (2H, H^{32}-*endo* + H^{32}-*exo*), 2.82 d.d (1H, H^{10a2}, ^2J 18, $^3J_{a,a'}$ 9 Hz), , 3.29 d.d (1H, H^{10e2}, ^2J 18, $^3J_{a,e'}$ 4 Hz), 3.56 s (3H, $COOCH_3$), 3.58d (1H, H^{8a2}, $^3J_{a,a'}$ 9 Hz), 3.96 t.d (1H, H^{9a}, 2 $^3J_{a,a'}$ 9, $^3J_{a,e'}$ 4 Hz), 4.86 br.d (1H, H^{112}, ^3J 9.6, 2 $^4J_{3',11'}$ 2 Hz), 5.14 d (1H, H^{12}, ^3J 9.6 Hz), 5.98 s (2H, OCH_2O), 6.76 m (2H_{arom}), 6.91 s (1H_{arom}), 7.15 d (1H, H^5, ^3J 9 Hz), 7.31 t and 7.44 t (1H each, H^2 and H^3, ^3J 7 Hz), 7.68 d and 7.76 d (1H each, H^1 and H^4, ^3J 7 Hz), 7.85 d (1H, H^6, ^3J 9 Hz), 9.58 s (1H, NH).

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