Heteroatom Chemistry
Volume 16, Number 7, 2005

The Povarov Reaction of Cyclopentadiene with Imines from Methyl 12-Amino-Dehydroabietate

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Received 19 July 2005

ABSTRACT: *The aza-Diels-Alder cycloaddition reaction of cyclopentadiene with benzylideneanilines from methyl 12-amino-dehydroabietate is described via the Povarov reaction.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:605–612, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20159

INTRODUCTION

The Povarov reaction is a powerful and efficient means for the construction of tetrahydroquinoline core of Schiff bases (from substituted anilines and various aldehydes) with cyclic and acyclic alkylvinyl ethers [1], cyclic dienes (the Grieco reaction) [2], olefins [3], or enamines [4]. This reaction is formally regarded as the [4+2]-aza-Diels-Alder cycloaddition between activated olefin and Schiff base in which the latter component serves as the 2-azadiene, and is promoted by Lewis acids ($BF_3{\cdot}OEt_2$, $InCl_3$) [5], Brönsted acids (CF_3COOH, TsOH) [6], lanthanide triflates [7], urea nitrate [8], samarium(II) iodide [9], and triphenylphosphonium perchlorate [10]. Principles of the Povarov reaction were used for the synthesis of pyrroloquinoline core of martinelline—alkaloid from the roots of the Amazonian plant *Martinella iquitosensis* [1g,11].

Despite the utility of the Povarov reaction, we decided to apply this reaction for Schiff bases from tricyclic diterpenoids. We continue our studies of heterocyclic compounds [12], and here we report the Povarov reaction of cyclopentadiene with imines **2a–c** from methyl 12-aminodehydroabietate **1** and aromatic aldehydes (Scheme 1). The formation of condensed tetrahydroquinolines **3a–c** is successfully catalyzed by CF_3CO_2H or $BF_3{\cdot}OEt_2$ (Scheme 2). It is pertinent to note that nitrogen-containing heterocyclic derivatives of tricyclic diterpenoids [13] are a subject of much current interest as a biologically active substances, for instance, dehydroabietic acid derivatives of imidazole [14], pyrrole, and piperazine [15], as well as some phenanthreno[9,10-*b*]indoles with pronounced antiviral activity [16].

RESULTS AND DISCUSSION

Schiff bases **2a–e** were easily obtained with good yields from methyl 12-aminodehydroabietate [17]

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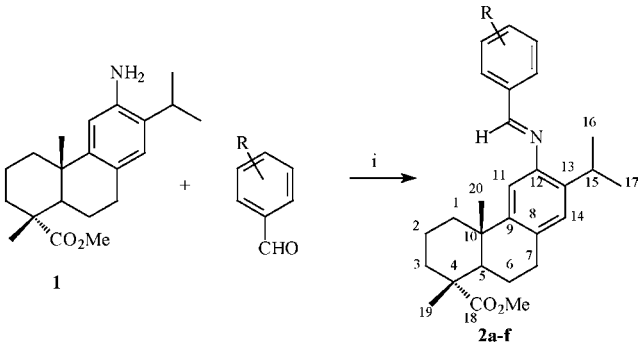
and an appropriate aromatic aldehyde in methanol (benzene, or toluene) at room temperature, in the presence of molecular sieves 4 Å (Scheme 1, Table 1).

The structure of **2a–g** is supported by IR and ^{1}H NMR data (Table 2). IR spectra of compounds **2a–g** showed bands 1705–1720 cm^{-1} and 1615–1625 cm^{-1} characteristic of ester carbonyl and C=N bond, respectively. Proton shifts interpretation in the NMR spectra of **2a–f** was conducted in accordance with the publication [18]. The ^{1}H NMR spectra of compounds **2a–f** showed only one signal of N=CH group for each compound at 8.20–8.40 ppm, thus indicating only one isomer, presumably, *trans*-stereoisomer in all cases. In order to examine absolute configuration of **2b**, the X-ray analysis of its single crystal was performed (Fig. 1).

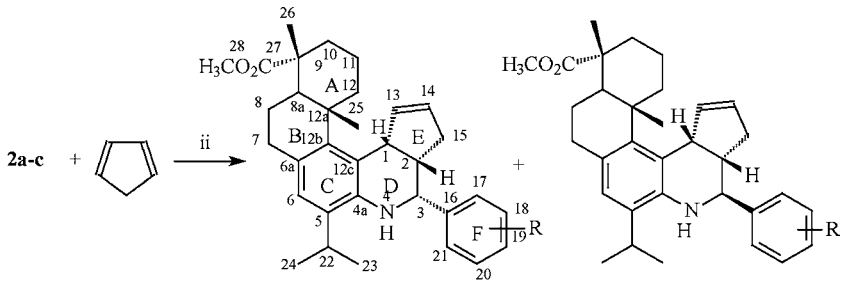


2 a: R = H, **b**: R = 3-NO_2, **c**: R = 4-CF_3, **d**: R = 4-NO_2, **e**: R = 4-Cl, **f**: R = 4-Br; **g**: R = 4-CH_3O

i: benzene, toluene or methanol, 20 °C, molecular sieves 4Å

SCHEME 1

The ORTEP view of molecule **2b** is depicted in Fig. 1. The cyclohexane fragment is characterized by chair conformation. Substituents at C(4) atom are located so that methyl group adopts axial position while more bulky ester group adopts equatorial one. The conformation of the cyclohexene ring can be described as distorted half-chair. The torsion angle at the C(8)=C(9) double bond is close to zero and C(7)–C(8)–C(9)–C(10) is 6.7(4)°), while the C(6)–C(7)–C(8)–C(9) and C(8)–C(9)–C(10)–C(5) torsion angles are −21.9(4) and



ii: $BF_3 \cdot OEt_2$, 20 mol %, or CF_3COOH, 1 eq., MeCN, 20 °C, 12-36 h

SCHEME 2

TABLE 1 Physical and Chemical Characteristics and Data Analysis for Synthesized Compounds

	Molecular Formula	*Found, Calculated (%)*			*mp (°C)*	*$[\alpha]_D^{23}$, (°) (c 1, $CHCl_3$)*	*Yield (%)*
		C	*H*	*N*			
2a	$C_{28}H_{35}NO_2$	80.32, 80.54	8.56, 8.48	3.28, 3.35	Oil	+144.1	53
2b	$C_{28}H_{34}N_2O_4$	72.66, 72.70	7.52, 7.41	5.98, 6.06	106–107	+176.5[a]	52
2c	$C_{29}H_{34}F_3NO_2$	71.44, 71.73	7.14, 7.06	2.73, 2.88	118–119	+90.4	43
2d	$C_{28}H_{34}N_2O_4$	72.42, 72.70	7.41, 7.41	5.85, 6.06	215–216	+149.3	63
2e	$C_{28}H_{34}ClNO_2$	74.37, 74.40	7.94, 7.58	3.08, 3.10	137–139	+108.4	56
2f	$C_{28}H_{34}BrNO_2$	67.58, 67.74	7.02, 6.90	2.77, 2.82	138–140	+204.2[a]	59
2g	$C_{29}H_{37}NO_3$	77.66, 77.82	8.45, 8.33	3.07, 3.13	138–140	+177	59
3a	$C_{33}H_{41}NO_2$	81.89, 81.95	8.55, 8.54	2.76, 2.90	Oil	–	63 (method A) 45 (method B)
3b	$C_{33}H_{40}N_2O_4$	74.71, 74.97	7.74, 7.63	5.17, 5.30	110–111	–	50 (method A) 60 (method B)
3c	$C_{34}H_{40}F_3NO_2$	74.34, 74.02	7.24, 7.31	2.45, 2.54	Oil	–	89 (method A) 56 (method B)

[a] $[\alpha]_{578}^{23}$.

TABLE 2 ^{1}H NMR, IR, and Mass-Spectra Data for Compounds **2a–f, 3a–c**

Compound	*^{1}H NMR Data*	*IR Data (ν, cm^{-1})*	*Mass-Spectra Data e/z, (RI ,%)*
2a	1.09 (d, 3 H, CH_3, $J = 7$ Hz); 1.14 (d, 3 H, CH_3, $J = 7$ Hz); 1.18 (s, 3 H, $H_3C(20)$); 1.21 (s, 3 H, $H_3C(19)$); 1.37–1.90 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.22 (m, 2 H, HC(5) and β-HC(1)); 2.85 (m, 2 H, $H_2C(7)$); 3.37 (m, 1 H, HC(15)); 3.60 (s, 3 H, CH_3O; 6.70 (s, 1 H, HC(14)); 6.87 (s, 1 H, HC(11)); 7.39 (m, 3 H, Ph); 7.85 (m, 2 H, Ph); 8.28 (s, 1 H, NCH=)	1720 (O–C=O), 1620 (C =N), 1570, 1305, 1250, 1190, 1050, 1030, 1000, 900, 860	–
2b	1.12 (d, 3 H, CH_3, $J = 7$ Hz); 1.15 (d, 3 H, CH_3, $J = 7$ Hz); 1.19 (s, 3 H, $H_3C(20)$); 1.22 (s, 3 H, $H_3C(19)$); 1.35–1.86 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.24 (m, 2 H, HC(5) and β-HC(1)); 2.85 (m, 2 H, $H_2C(7)$); 3.38 (m, 1 H, HC(15)); 3.61 (s, 3 H, CH_3O; 6.74 (s, 1 H, HC(14)); 6.91 (s, 1 H, HC(11)); 7.59 (m, 1 H, 6′-H); 8.22 (m, 2 H, 4′,5′-H); 8.39 (s, 1 H, NCH=); 8.65 (s, 1 H, 2′-H)	1705 (O–C=O), 1615 (C=N), 1525 (NO_2), 1340 (NO_2), 1240, 1180, 1135, 1100, 1075, 1045, 1020, 1000, 890	–
2c	1.12 (d, 3 H, CH_3, $J = 7$ Hz); 1.16 (d, 3 H, CH_3, $J = 7$ Hz); 1.19 (s, 3 H, $H_3C(20)$); 1.22 (s, 3 H, $H_3C(19)$); 1.35–1.86 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.20 (dd, 1 H, HC(5), $J_1 = 12.3$ Hz; $J_2 = 1.8$ Hz); 2.26 (m, 1 H, β-HC(1)); 2.85 (m, 2 H, $H_2C(7)$); 3.36 (m, 1 H, HC(15)); 3,61 (s, 3 H, CH_3O; 6.73 (s, 1 H, HC(14)); 6.90 (s, 1 H, HC(11)); 7.65 (d, 2 H, 2′,6′-H, $J = 8.4$ Hz); 7.96 (d, 2 H, 3′,5′-H, $J = 8.4$ Hz); 8.34 (s, 1 H, NCH=)	1705 (O–C=O), 1620 (C=N), 1325, 1250, 1170, 1135, 1070, 1020, 995, 900, 860, 845	485 (M^+, 100), 410 (26), 289 (15), 288 (78), 144 (10)
2d	1.12 (d, 3 H, CH_3, $J = 7$ Hz); 1.16 (d, 3 H, CH_3, $J = 7$ Hz); 1.19 (s, 3 H, $H_3C(20)$); 1.22 (s, 3 H, $H_3C(19)$); 1.35–1.86 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.18 (m, 1 H, HC(5)); 2.26 (m, 1 H, β-HC(1)); 2.85 (m, 2H, $H_2C(7)$); 3.39 (m, 1 H, HC(15)); 3.61 (s, 3 H, CH_3O; 6.76 (s, 1 H, HC(14)); 6.91 (s, 1 H, HC(11)); 8.01 (d, 2 H, 2′,6′-H, $J = 8.7$ Hz); 8.27 (d, 2 H, 3′,5′-H, $J = 8.7$ Hz); 8.40 (s, 1 H, NCH=)	1710 (O–C=O), 1590 (C=N), 1510, 1345, 1250, 1170, 1135, 885, 860, 645	463 ($(M+1)^+$, 32), 462 (M^+, 100), 387 (30), 266 (13), 265 (67)
2e	1.11 (d, 3 H, CH_3, $J = 7$ Hz); 1.13 (d, 3 H, CH_3, $J = 7$ Hz); 1.18 (s, 3 H, $H_3C(20)$); 1.21 (s, 3 H, $H_3C(19)$); 1.30–1.80 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.21 (m, 2 H, β-HC(1) and HC(5)); 2.82 (m, 2 H, $H_2C(7)$); 3.33 (m, 1 H, HC(15)); 3,60 (s, 3 H, CH_3O; 6.70 (s, 1 H, HC(14)); 6.88 (s, 1 H, HC(11)); 7.39 (d, 2 H, 3′,5′-H, $J =$ 8.4 Hz); 7.78 (d, 2 H, 2′,6′-H, $J = 8.4$ Hz); 8.25 (s, 1 H, NCH=)	1715 (O–C=O), 1620 (C=N), 1245, 1130, 1010, 830	–
2f	1.12 (d, 3 H, CH_3, $J = 7$ Hz); 1.15 (d, 3 H, CH_3, $J = 7$ Hz); 1.18 (s, 3 H, $H_3C(20)$); 1.20 (s, 3 H, $H_3C(19)$); 1.32–1.83 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.20 (m, 2 H, HC(5) and β-HC(1)); 2.82 (m, 2 H, $H_2C(7)$); 3.37 (m, 1 H, HC(15)); 3.59 (s, 3 H, CH_3O; 6.66 (s, 1 H, HC(14)); 6.84 (s, 1 H, HC(11)); 7.52 (dd, 2 H, 3′,5′-H, $J =$ 7 Hz, $J = 1.5$ Hz,); 7.96 (dd, 2 H, 2′,6′-H, $J = 7$ Hz, $J =$ 1.5 Hz,); 8.23 (s, 1 H, NCH=)	1720 (O–C=O), 1625 (C=N), 1580, 1300, 1245, 1195, 1175, 1140, 1105, 1070, 1015, 980, 890, 860, 830	453 ($(M+2)^+$, 38), 452 ($(M+1)^+$, 32), 451 (M^+ 100), 376 (20), 256 (23), 255 (13), 254 (67), 144 (12)
2g	1.10 (d, 3 H, CH_3, $J = 7$ Hz); 1.15 (d, 3 H, CH_3, $J = 7$ Hz); 1.18 (s, 3 H, $H_3C(20)$); 1.21 (s, 3 H, $H_3C(19)$); 1.37–1.85 (m, 7 H, α-HC(1), $H_2C(2)$, $H_2C(3)$, $H_2C(6)$); 2.26 (m, 2 H, HC(5) and β-HC(1)); 2.82 (m, 2 H, $H_2C(7)$); 3.33 (m, 1 H, HC(15)); 3.60 (s, 3 H, CH_3O; 3.81 (s, 3 H, CH_3O; 6.68 (s, 1 H, HC(14)); 6.86 (s, 1 H, HC(11)); 6.91 (d, 2 H, 3′,5′-H, $J = 9$ Hz,); 7.79 (d, 2 H, 2′,6′-H, $J = 9$ Hz,); 8.20 (s, 1 H, NCH=)	1720 (O–C=O), 1620 (C=N), 1250, 1150, 1040, 880	–

(Continued)

TABLE 2 Continued

Compound	*^{1}H NMR Data*	*IR Data (ν, cm^{-1})*	*Mass-Spectra Data e/z, (RI ,%)*
3a	3-(*S*)-**3a**. 0.80–1.80 (m, 20 H, HC(2), α-HC(12), $H_2C(8)$, $H_2C(10)$, $H_2C(11)$, $H_3C(23)$, $H_3C(24)$, $H_3C(25)$, $H_3C(26)$); 2.10 (m, 1 H, C(15)H); 2.20 (m, 2 H, HC(8a), HC(15)H); 2.85 (m, 3 H, β-HC(12), $H_2C(7)$); 3.17 (m, 1 H, HC(22)); 3.62 (s, 3 H, OCH_3)); 3.81 (br s, 1 H, NH); 3.96 (d, 1 H, C(3)H, $J = 8.4$ Hz); 4.82 (m, 1 H, C(1)H); 5.06 (m, 1 H, HC(13)); 5.61 (m, 1 H, HC(14)); 6.62 (s, 1 H, HC(6)); 7.18–7.34 (m, 5 H, Ph). 3-(*R*)-**3a.** 0.80–1.80 (m, 20 H, HC(2), α-HC(12), $H_2C(8)$, $H_2C(10)$, $H_2C(11)$, $H_3C(23)$, $H_3C(24)$, $H_3C(25)$, $H_3C(26)$); 2.10 (m, 1 H, C(15)H); 2.20 (m, 2 H, C(8a)H, HC(15)); 2.85 (m, 3 H, β-HC(12), $H_2C(7)$); 3.17 (m, 1 H, HC(22)); 3.62 (s, 3 H, OCH_3)); 3.81 (br s, 1 H, NH); 3.90 (d, 1 H, C(3)H, $J = 8.4$); 4,75 (m, 1 H, C(1)H); 5.34 (m, 1 H, HC(13)); 5.74 (m, 1 H, HC(14)); 6.67 (s, 1 H, HC(6)); 7.18–7.34 (m, 5 H, Ph).	3250 (NH), 1705 (C=O), 1610 (C=C), 1520 (C=C_{arom})	–
3c	3-(*S*)-**3c**. 0.79–1.75 (m, 20 H, HC(2), α-HC(12), $H_2C(8)$, $H_2C(10)$, $H_2C(11)$, $H_3C(23)$, $H_3C(24)$, $H_3C(25)$, $H_3C(26)$); 1.96 (m, 1 H, C(8a)H), 2.10 (m, 1 H, C(15)H); 2.20 (m, 1 H, HC(15)); 2.80–2.90 (m, 3 H, β-HC(12), $H_2C(7)$); 3.19 (m, 1 H, HC(22)); 3.64 (s, 3 H, OCH_3)); 3.85 (br s, 1 H, NH); 4.02 (d, 1 H, C(3)H, $J = 5.1$ Hz); 4.62 (m, 1 H, C(1)H); 5.28 (m, 1 H, HC(13)); 5.67 (m, 1 H, HC(14)); 6.84 (s, 1 H, HC(6)); 7.59 (d, 2 H, 3′,5′-H, $J =$ 8.4 Hz); 7.90 (d, 2 H, 2′,6′-H, $J = 8.4$ Hz). 3-(*R*)-**3c.** 0.79–1.75 (m, 20 H, HC(2), α-HC(12), $H_2C(8)$, $H_2C(10)$, $H_2C(11)$, $H_3C(23)$, $H_3C(24)$, $H_3C(25)$, $H_3C(26)$); 2.10 (m, 1 H, C(15)H); 2.18 (m, 1 H, C(8a)H), 2.20 (m, 1 H, HC(15)); 2.80–2.90 (m, 3 H, $H_2C(12)$, $H_2C(7)$); 3.19 (m, 1 H, HC(22)); 3.64 (s, 3 H, OCH_3)); 3.84 (m, 2 H, C(3)H + NH); 4.86 (m, 1 H, C(1)H); 5.07 (m, 1 H, HC(13)); 5.60 (m, 1 H, HC(14)); 6.64 (s, 1 H, HC(6)); 7.45 (d, 2 H, 2′,6′-H, $J = 8.4$ Hz), 7.59 (d, 2 H, 3′,5′-H, $J = 8.4$ Hz).	3230 (NH), 1700 (C=O), 1620 (C=C), 1515 (C=C_{arom})	–

[a]IR spectrum of compound **2b** (ν, cm^{-1}): 3200 (NH), 1690 (C=O), 1635 (C=C), 1570 (NO_2), 1520 (C=C_{arom}), 1335 (NO_2), 1230, 1125, 1050.

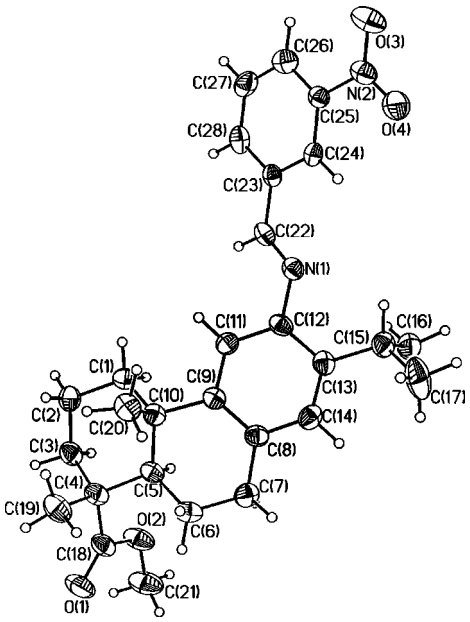


FIGURE 1 ORTEP view (50%) of molecule **2b**.

−20.9(4)°, respectively. The NO_2—Ph—N=C—Ph fragment is not planar. The nitro group as well as N=C fragment appears to be coplanar with the C(23)–C(24)–C(25)–C(26)–C(27)–C(28) benzene ring (torsion angles C(24)–C(25)–N(2)–O(4) and C(24)–C(23)–C(22)–N(1) are 0.2(4) and 2.2(5)°, respectively) which imply π-conjugation in this planar fragment (mean deviation is 0.018 Å) while the other benzene ring is twisted out of that plane: the C(11)–C(12)–N(1)–C(22) torsion angle is equal to −38.1(4)°. Bond lengths in **2b** are in the range of normally observed ones [19,20].

In the crystal, molecules are assembled in the columns in which molecules are related by screw axis along *a* crystallographic direction (Fig. 2a). Columns are formed by strong stacking interaction between adjacent molecules. The C(23)–C(24)–C(25)–C(26)–C(27)–C(28) benzene rings are involved in a stacking interaction being partly (about half) projected onto each other (Fig. 2b). Interplanar

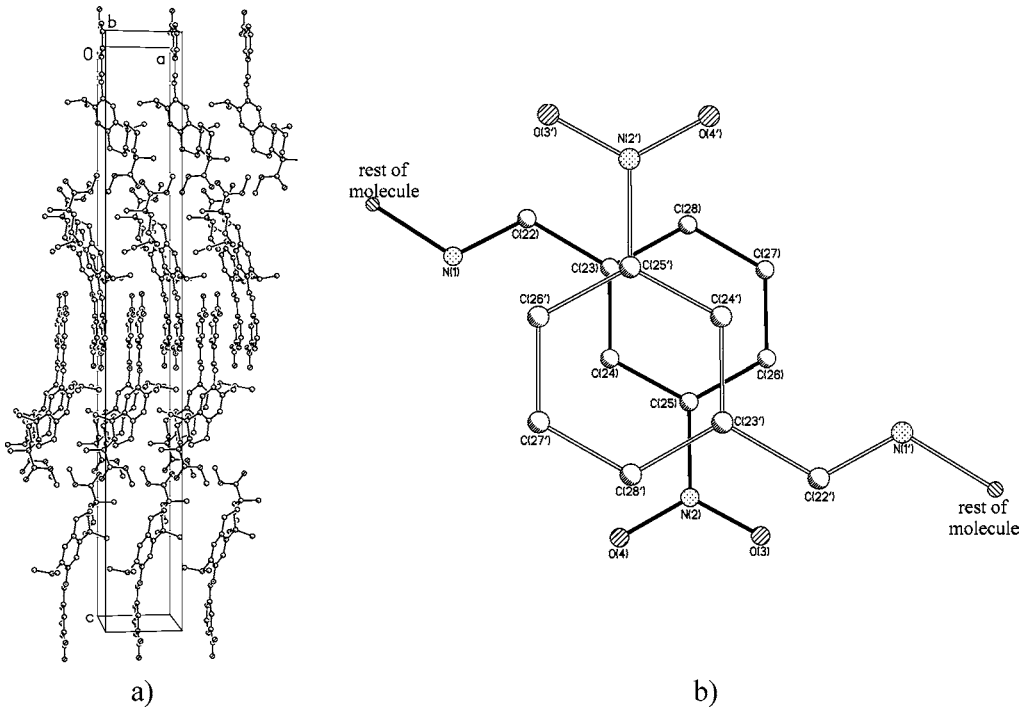


FIGURE 2 Crystal structure of the compound **2b**. (a) Fragment of crystal packing as projection onto *ac* plane. (b) Stacking interaction between [*x*, *y*, *z*] and [0.5 + *x*, 0.5 − *y*, −*z*] (denoted by primed atomic labels and open bond lines); only necessary molecular fragments are shown.

angle is 1.80(1)°, interplanar distance (calculated as an average value of the deviation of the carbon atoms of benzene ring from the average plane of the adjacent benzene ring) appears as short as 3.152(6) Å, while the closest interatomic distances are C(23)···C(25a), 3.185(4) Å and C(25)···C(23a), 3.219(4) Å.

We examined the Povarov cycloaddition reaction of cyclopentadiene with benzylideneanilines **2a–f** (Scheme 2). At first, different catalysts (BF_3·OEt2, CF_3COOH, $ZnCl_2$, squaric acid, $Yb(OTf)_3$·H2O) were tested for the compound **2b**. The best yields were obtained with boron trifluoride etherate and trifluoroacetic acid, so these substances were the catalysts of our choice (Table 1).

^{1}H NMR spectra of tetrahydroquinolines **3a–c** indicate that two stereoisomers at the C(3) atom are formed in the reaction: 3-(*S*)-**3** and 3-(*R*)-**3** (Scheme 2, Table 2). Ratio 3-(*R*)-**3b**/3-(*S*)-**3b** is 1.65:1. The compound **3b** was studied intensively by NMR methods. The ^{1}H NMR spectrum of the compound **3b** was assigned using 2D ^{1}H, ^{1}H COSY, and TOCSY spectra. The ^{13}C NMR spectrum was assigned using 2D ^{1}H, ^{13}C HSQC, and HMBC spectra (Table 3).

Some important nontrivial NOE contacts characteristic of both isomer 3-(*R*)-**3b** and isomer 3-(*S*)-**3b** are H-1/H-2 (an evidence of *cis*-orientation of the protons) and H-25/H-1; H-13/H-12$_{ax}$ (strong) and H-13/H-12$_{eq}$ (weak) (evidences of *cis*-joint of the cycles D and E shown in Scheme 2). Some strong nontrivial NOE contacts characteristic of isomer 3-(*R*)-**3b** only are H-17/H-15 and H-21/H-15 (a demonstration of *cis*-orientation of the cycles E and F for the predominant isomer 3-(*R*)-**3b**).

Our attempt to separate isomers 3-(*R*)-**3b** and 3-(*S*)-**3b** by HPLC on Daicel chyralcel OD column (liquid phase–hexane +0.05% ^{i}PrOH) was failed.

Compounds **2d–f** are unable to complete the cycloaddition reaction with cyclopentadiene. Probably, electron-rich groups at *para*-position of the aromatic ring reduced the electrophility of C-atom of imino-group, which is responsible for nucleophilic attack of dienophile [4,7a]. Compound **2d** also failed to react, though reason is unknown.

TABLE 3 ^{13}C and ^{1}H NMR Data (δ, ppm) of the Isomers 3-(*R*)-**3b** and 3-(*S*)-**3b**

Atom	*3-(R)*-**3b**	*3-(S)*-**3b**	*Atom*	*3-(R)*-**3b**	*3-(S)*-**3b**
1	47.4	46.4	12c	126.3	127.3
	4.83	*4.75*			
2	45.8	44.4	13	133.6	134.5
	3.34	*3.24*		*5.03*	*5.31*
3	61.7	61.3	14	129.2	130.1
	4.12[a]	*4.05*[b]		*5.57*	*5.67*
4 (NH)	*4.30*	*4.09*	15	33.4	34.0
				2.16; 2.02	*2.13; 2.06*
4a	145.7	146.0	16	144.3	144.4
5	131.5	132.4	17	121.6	121.4
				8.30	*8.24*
6	123.1	124.1	18	147.8	147.8
	6.59	*6.64*			
6a	126.1	126.3	19	121.5	121.6
				8.15	*8.15*
7	31.6	33.1	20	129.6	129.6
	2.77; 2.71	*2.81; 2.64*		*7.68*	*7.67*
8	21.4	22.2	21	133.6	133.4
	1.70; 1.20	*1.60; 1.17*		*7.80*	*7.86*
8a	48.0	48.5	22	25.3	25.5
	1.96	*2.18*		*3.06*	*3.04*
9	47.8	48.3	23	22.4	22.3
				1.11	*1.10*
10	35.9	35.5	24	22.7	22.7
	1.70; 1.68	*1.76; 1.63*		*1.06*	*1.05*
11	18.4	18.6	25	20.8	22.1
	1,78; 1.63	*1.77; 1.60*		*1.44*	*1.46*
12	38.3	38.7	26	17.2	16.9
	2.88; 1.40	*2.68; 1.50*		*1.26*	*1.22*
12a	37.6	39.0	27	178.0	178.1
12b	143.8	143.6	28	51.8	51.8
				3.61	*3.64*

Italic figures belong to chemical shifts of the corresponding attached protons.
[a] $J_{3,2}$ 4.7 Hz.
[b] $J_{3,2}$ 5.5 Hz.

CONCLUSIONS

Starting from methyl 12-amino-dehydroabietate, a number of Schiff bases **2a–g** were synthesized. The aza-Diels-Alder cycloaddition reaction of cyclopentadiene with the compounds **2a–g**, catalyzed by BF_3·OEt2 and CF_3COOH, was examined. It was shown that the possibility of cyclocondensation reaction depends on the nature of substituents in the aromatic ring.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a UR-20 in Nujol. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian mercury plus 300 (300 MHz), ^{1}H and ^{13}C spectra of isomers 3-(*R*)-**3b** and 3-(*S*)-**3b** were recorded on a Bruker DRX-500 spectrometer at 30°C and with $CDCl_3$ as solvent. 2D NMR experiments were performed using standard Bruker software. A mixing time of 300 ms was used in ROESY experiment, and a delay of 60 ms in an HBMC experiment. Elemental analyses (C,H,N) were carried out on a Carlo Erba model 1106 elemental analyzer, and the results are within ±0.4% of the theoretical values. Mass-spectra of compounds **2c,d,f** were recorded on a Finnigan MAT instrument under standard conditions (EI, 70 eV). Optical rotations were measured with a Perkin–Elmer 341 polarimeter and are given in a deg dm^{-1} g^{-1} mL. Column chromatography was carried out on silica gel 60 (Merck, 80–230 mesh). For analytical TLC 0.2 mm Merck 60 silica gel plates were used, and hexane–EtOAc (10:1) as an eluent, detected with saturated ethanolic solution of phosphomolybdic acid at 120–150°C.

General Procedure for Synthesis of Imines **2a–g**

Methyl 12-amino-dehydroabietate (329 mg, 1 mmol) [17] and 1 g of molecular sieves 4 Å were added to a solution of aromatic aldehyde (1 mmol) in 30 mL of dry benzene (toluene or methanol). The reaction mixture was stirred for 12–36 h at room temperature. The reaction is monitored by TLC. Molecular sieves were separated, crushed in a mortar, washed with 10 mL of an acetonitrile, and the solvent was evaporated in vacuo; the crude product was crystallized from ethanol. In the case of compounds **2a,c** crude products were purified by column chromatography on silica gel 60 (eluent hexane–EtOAc, 10:1), then compound **2c** was recrystallized from ethanol.

General Procedure for Synthesis of 3-Aryl-9,12a-dimethyl-5-isopropyl-9-methoxycarbonyl-1,2-(1-propenylene)-1,2,3,4,7,8,8a,9,11,12,12a-dodecahydro-naphtho[1,2-f]quinolines **3a–c**

Method A. To the compound **2a–c** (1 mmol) and 0.33 mL (264 mg, 4 mmol) of freshly distilled cyclopentadiene, dissolved in 80 mL of dry acetonitrile, 0.5 mL (6.5 mmol) of CF_3COOH and 1 g of molecular sieves 4 Å were added. The reaction mixture was stirred at room temperature for 12–36 h (TLC control), evaporated in vacuo; then sat. aq. $NaHCO_3$ (20 mL) was added and the product was extracted by EtOAc (30 mL ×3), treated by brine and dried over $MgSO_4$. The crude product was purified by chromatography on silica gel to afford compounds **3a–c** (hexane–EtOAc, gradient elution from 100 to 80% hexanes, v/v). Compound **3b** was recrystallized from methanol.

Method B. The reaction is conducted in the same way, but instead of CF_3COOH $BF_3{\cdot}OEt2$ was added (0.026 mL, 29 mg, 0.2 mmol, 20 mol%).

X-ray Crystallography. X-Ray quality crystals of the compound **2b** were grown by crystallization from ethanol at 25°C. The single crystals of **2b** ($C_{28}H_{34}N_2O_4$) are orthorhombic, space group $P2_12_12_1$: $a = 6.340(2)$ Å, $b = 7.968(2)$ Å, $c = 49.249(11)$ Å, $V = 2488.1(10)$ Å^3, $Z = 4$, $M = 462.57$, $d_{calc} = 1.235$ g cm^{-3}, $\mu = 0.082$ mm^{-1}. Carefully chosen sample (0.1 × 0.05 × 0.05 mm) has been used for the X-ray study. 22009 reflections were collected at SMART 1000 CCD diffractometer (λ(Mo Kα) = 0.71073 Å, graphite monochromator, ω-scans, $2\theta < 52^\circ$) at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation. All the hydrogen atoms were placed in geometrically calculated positions and refined within riding model. 4897 independent reflections were used in the refinement procedure (for 312 parameters) that was converged to $wR_2 = 0.1122$ calculated on F^2_{hkl} (GOF = 1.001, $R_1 = 0.0596$ calculated on F_{hkl} using 2967 reflections with $I > 2\sigma(I)$). For the analysis of data collected and crystal structures refinement, we used SAINT Plus [21], SADABS [22], and SHELXTL-97 [23] program packages. Information obtained for the crystal structure of **2b** has been deposited at the Cambridge Crystallographic Data Centre, with the number 277459.

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