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Synthesis of Aromatic Azomethines by Condensation of Substituted Benzaldehydes with 4-Aminophenylene-*N*-imide of Maleopimaric Acid

E. A. Dikusar[a,b], M. P. Bei[b], A. P. Yuvchenko[b], and V. I. Potkin[a]

[a] *Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, ul. Surganova 13, Minsk, 198013 Belarus*
e-mail: dikusar@ifoch.bas-net.by

[b] *Institute of Chemistry of New Materials, National Academy of Sciences of Belarus, Minsk, Belarus*

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Abstract—Preparative method of synthesis of aromatic azomethines by condensation of substituted benzaldehydes of vanillin series with 4-aminophenylene-*N*-imide of maleopimaric acid was developed.

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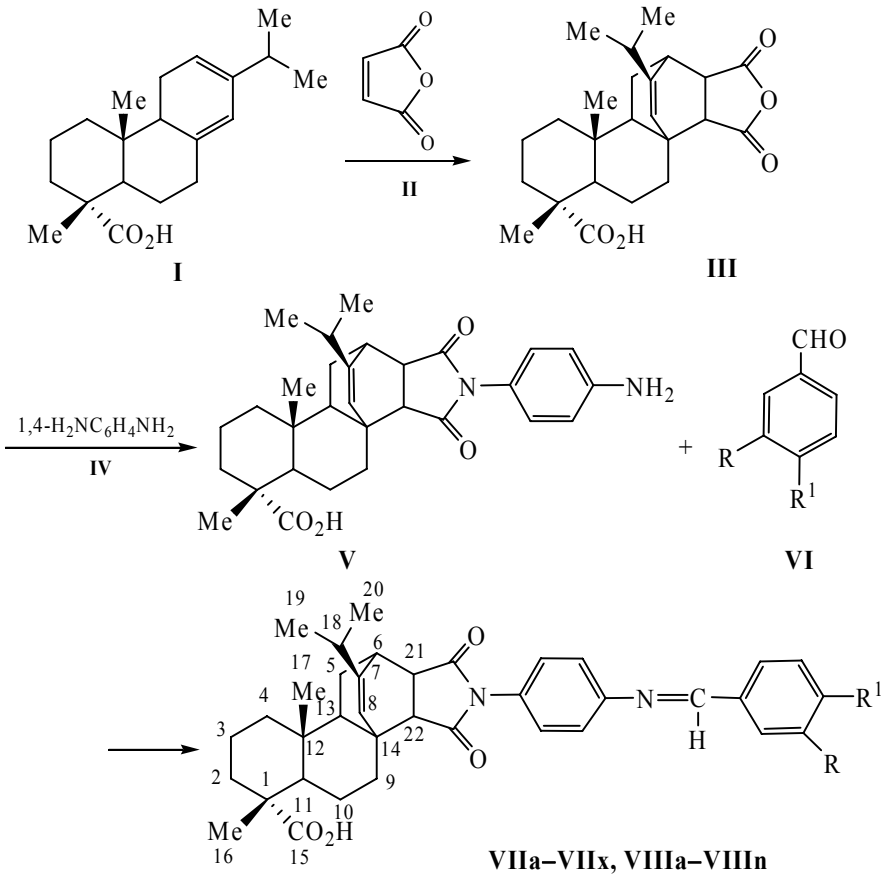
Levopimaric acid **I** is a constituent of turpentine obtained from a gum of coniferous trees, in particular, from pine (*Pinus Silvestris L.*) [1]. Maleopimaric acid **III** is a diene adduct, which forms by Diels-Alder reaction from levopimaric acid **I** and maleic anhydride **II** [2–10]. Maleopimaric acid **III** is convenient and accessible synthon for preparation of compounds possessing wide spectrum of biological, anti-inflammatory, nematocidal, and fungicidal activity [6-10], and also for monomer synthesis [11, 12]. The high biological activity of maleopimaric acid derivatives is caused by stereochemical features of their 13α-configuration, which resembles by the structure the stereochemistry of A, B, and C rings of steroid hormones [4, 13].

In this work a new preparative approach to 4-aminophenylene-*N*-imide of maleopimaric acid **V** was developed on the basis of reaction of maleopimaric acid **III** with 4-phenylenediamine **IV** in toluene under reflux. The obtained compound **V** contains reactive amino group and may be used as a suitable synthon for synthesis of aromatic azomethines. 4-Aminophenylene-*N*-imide of maleopimaric acid **V** we succeeded to introduce into condensation with substituted benzaldehydes of vanillin series **VI** to obtain functionally substituted aromatic azomethines containing maleopimaric acid fragment **VIIa–VIIx**, **VIIIa–VIIIn**. The reaction was carried out by refluxing the mixture of starting materials (with the use of stochiometric ratio of compounds **V** and **VI**, 1:1) in the mixture of anhydrous methanol and dimethylformamide (1:1) for 3–4 h. Yields of azomethines **VIIa–VIIx, VIIIa–VIIIn** were 78–88%.

Azomethines **IIIa–IIIx** and **IVa–IVn** are crystalline substances, soluble in DMF, DMSO and insoluble in methanol, diethyl ether, chloroform, and hydrocarbons. Their structure was proved by IR and ^{1}H NMR spectroscopy, elemental analysis data (see the table). According to the ^{1}H NMR data, the purity of the obtained compounds is 92±1%.

The IR spectra of azomethines **IIIa–IIIx** and **IVa–IVn** contain the following characteristic absorption bands (ν, cm^{-1}): OH_{acid} 2200–3600; CH_{Ar} 3080–3005, 870–650; $CH_{aliphatic}$ 2995–2830; C=O 1780–1620; C=N 1630–1625; $C=C_{Ar}$ 1600±5, 1515±2, 1388±2; CO 1290–1002. In the IR spectrum of compound **IIIs** the presence of NO_2-group was confirmed by characteristic absorption bands in the region of 1534 and 1351 cm^{-1}. The IR spectra of carborane-containing azomethines **IIIw, IIIx, IVm,** and **IVn** contain the following absorption bands: $CH_{carb.}$ 3070 (**IIIw, IVm**), 3034 (**IIIx, IVn**); BH 2680–2657 cm^{-1}.

In the ^{1}H NMR spectra of azomethines **IIIa–IIIx** and **IVa–IVn** the signals of protons of maleopimaric acid fragment appear in the following ranges (δ, ppm): 0.64-0.56 s (3H, MeC^{12}), 0.96–0.94 d (6H, Me_2C^{18}), 1.05–1.18 s (3H, MeC^{1}), 5.35–5.55 br. s (1H, C=CH),



VII, R = R^1 = H (**a**); R = H, R^1 = MeO (**b**); R = MeO, R^1 = HO (**c**), MeO (**d**), MeC(O)O (**e**), EtC(O)O (**f**), PrC(O)O (**g**), $Me_2CHC(O)O$ (**h**), BuC(O)O (**i**), $Me_2CHCH_2C(O)O$ (**j**), $Me(CH_2)_6C(O)O$ (**k**), $Me(CH_2)_8C(O)O$ (**l**), $Me(CH_2)_{16}C(O)O$ (**m**), $H_2C{=}C(Me)C(O)O$ (**n**), $C_6H_5CH(Me)CH_2C(O)O$ (**o**), $C_6H_5C(O)O$ (**p**), 2,4-$Cl_2C_6H_3C(O)O$ (**q**), 4-$BrC_6H_4C(O)O$ (**r**), 3-$O_2NC_6H_4C(O)O$ (**s**), MeOC(O)O (**t**), EtOC(O)O (**u**), 1-AdC(O)O (**v**), *o*-$HCB_{10}H_{10}C(O)O$ (**w**), *m*-$HCB_{10}H_{10}C(O)O$ (**x**); **VIII**, R^1 = EtO, R^1 = HO (**a**), MeO (**b**), MeC(O)O (**c**), EtC(O)O (**d**), PrC(O)O (**e**), $Me_2CHC(O)O$ (**f**), BuC(O)O (**g**), $Me_2CHCH_2C(O)O$ (**h**), 4-$MeC_6H_4C(O)O$ (**i**), MeOC(O)O (**j**), EtOC(O)O (**k**), 1-AdC(O)O (**l**), *o*-$HCB_{10}H_{10}C(O)O$ (**m**), *m*-$HCB_{10}H_{10}C(O)O$ (**n**).

9.70–10.10 br.s (1H, COOH). In the ^{1}H NMR spectra of azomethines **IIIb–IIIx, IVb, VIa** the signals of MeO-group protons appear as singlets at 3.85–3.91 ppm. The ^{1}H NMR spectra of compounds **IVa–IVn** and **VIb** contain signals of EtO-group protons as a triplet at 0.90–1.30 ppm (Me) and a quartet at 3.80–4.20 ppm (CH_2). The signals of aromatic protons in compounds **IIIa–IIIx, IVa–IVn, V, VIa, VIb** are located in the range of 6.60–7.95 ppm. Azomethine protons HC=N appear as a singlet at 8.45–8.50 ppm, characteristic of *E*-configuration of azomethines [14].

In the IR and ^{1}H NMR spectra of azomethines **IIIa–IIIx** and **IVa–IVn** there are absorption bands and proton signals, which confirm the presence of the corresponding structural fragments of ester groups [15].

EXPERIMENTAL

The IR spectra were taken on an IR Fourier-spectrophotometer Protege-460 (Nicolet) using a film or pellets with KBr. The ^{1}H NMR spectra were registered on a Tesla BS-587A spectrometer (100 MHz) from 5% solution in DMSO-d_6, chemical shifts were determined relative to internal TMS. Elemental analysis was made on C, H, N, O, S-analyzer Vario EL-III Elementar, error 0.1%.

Esters of vanillin and vanillin aldehyde **VI** were obtained by procedures [16–21].

Yields, melting points, and elemental analysis data of azomerines **VIIa–VIIx, VIIIa–VIIIn**

Comp. no	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VIIa	87	270–271	77.12	7.43	4.52	$C_{37}H_{42}N_2O_4$	76.79	7.31	4.84
VIIb	88	232–233	75.19	7.32	4.29	$C_{38}H_{44}N_2O_5$	74.97	7.29	4.60
VIIc	78	240–241	73.24	7.29	4.20	$C_{38}H_{44}N_2O_6$	73.05	7.10	4.48
VIId	84	255–256	73.54	7.38	3.99	$C_{39}H_{46}N_2O_6$	73.33	7.26	4.39
VIIe	88	238–239	72.40	7.06	3.87	$C_{40}H_{46}N_2O_7$	72.02	6.95	4.20
VIIf	86	221–222	72.65	7.37	3.83	$C_{41}H_{48}N_2O_7$	72.33	7.11	4.11
VIIg	81	214–215	72.89	7.36	3.66	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIh	85	192–193	72.94	7.26	4.85	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIi	86	238–239	73.15	7.45	3.56	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIj	88	157–158	72.98	7.51	3.90	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIk	85	85–86	73.85	7.92	3.43	$C_{46}H_{58}N_2O_7$	73.57	7.78	3.73
VIIl	87	74–75	74.53	8.19	3.18	$C_{48}H_{62}N_2O_7$	74.01	8.02	3.60
VIIm	82	42–43	75.90	8.84	2.65	$C_{56}H_{78}N_2O_7$	75.47	8.82	314
VIIn	88	201–202	73.22	7.16	3.74	$C_{42}H_{48}N_2O_7$	72.81	6.98	4.04
VIIo	85	92–93	75.18	7.11	3.42	$C_{48}H_{54}N_2O_7$	74.78	7.06	3.63
VIIp	88	127–128	74.37	6.69	3.50	$C_{45}H_{48}N_2O_7$	74.15	6.64	3.84
VIIq[a]	86	104–105	68.02	5.90	3.14	$C_{45}H_{46}Cl_2N_2O_7$	67.75	5.81	3.51
VIIr[b]	82	184–185	67.34	5.93	3.11	$C_{45}H_{47}BrN_2O_7$	66.91	5.86	3.47
VIIs	85	181, decomp.	70.13	6.27	5.05	$C_{45}H_{47}N_3O_9$	69.84	6.12	5.43
VIIt	83	243–244	70.82	6.90	3.65	$C_{40}H_{46}N_2O_8$	70.36	6.79	4.10
VIIu	83	238–239	71.00	7.06	3.78	$C_{41}H_{48}N_2O_8$	70.67	6.94	4.02
VIIv	80	161–162	75.15	7.52	3.56	$C_{49}H_{58}N_2O_7$	74.78	7.43	3.56
VIIw[c]	83	>310	62.23	6.98	3.15	$C_{41}H_{54}B_{10}N_2O_7$	61.94	6.85	3.52
VIIx[d]	87	302–303	62.34	7.06	3.35	$C_{41}H_{54}B_{10}N_2O_7$	61.94	6.85	3.52
VIIIa	79	245–246	73.52	7.31	4.02	$C_{39}H_{46}N_2O_6$	73.33	7.26	4.39
VIIIb	80	257–258	73.84	7.57	3.92	$C_{40}H_{48}N_2O_6$	73.59	7.41	4.29
VIIIc	82	264–265	72.57	7.32	3.83	$C_{41}H_{48}N_2O_7$	72.33	7.11	4.11
VIIId	83	206–207	72.94	7.58	3.80	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIIe	88	117–118	73.10	7.61	3.48	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIIf	84	108–109	72.80	7.50	3.72	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIIg	85	105–106	73.43	7.65	3.61	$C_{44}H_{54}N_2O_7$	73.10	7.53	3.88
VIIIh	81	92–93	73.58	7.42	3.29	$C_{44}H_{54}N_2O_7$	73.10	7.53	3.88
VIIIi	79	124–125	75.03	7.13	3.25	$C_{47}H_{52}N_2O_7$	74.58	6.92	3.70
VIIIj	80	207–208	70.87	7.10	3.84	$C_{41}H_{48}N_2O_8$	70.67	6.94	4.02
VIIIk	82	211–212	71.36	7.18	3.51	$C_{42}H_{50}N_2O_8$	70.96	7.09	3.94
VIIIl	82	124–25	75.20	7.51	3.38	$C_{50}H_{60}N_2O_7$	74.97	7.55	3.50
VIIIm[e]	80	291–292	62.64	7.03	3.14	$C_{42}H_{56}B_{10}N_2O_7$	62.35	6.98	3.46
VIIIn[f]	82	296–297	62.45	7.17	3.22	$C_{42}H_{56}B_{10}N_2O_7$	62.35	6.98	3.46

[a] Found Cl, %: 8.51. Calculated Cl, %: 8.89. [b] Found Br, %: 9.55. Calculated Br, %: 9.89. [c] Found B, %: 13.19. Calculated B, %: 13.60.
[d] Found B, %: 13.28. Calculated B, %: 13.60. [e] Found B, %: 12.76. Calculated B, %: 13.36. [f] Found B, %: 12.97. Calculated B, %: 13.36.

4-Aminophenylene-*N*-imide of maleopimaric acid (V). A solution of 10 g (0.025 mol) of maleopimaric acid and 2.70 g (0.025 mol) of *p*-phenylenediamine was refluxed in toluene for 6 h. Reaction progress was monitored by TLC method using Silufol UV–254 plates, eluent hexane-acetone (2:1.6). Imide precipitate was filtered off, washed with toluene (10×2) and boiling water (50×2), dried in air. The boiling point of the obtained imidoacid **V** (309–310ºC) corresponds to literary data [22].

Functionally substituted aromatic azomethines (VIIa–VIIx, VIIIa–VIIIn). A mixture of 1 mmol of 4-aminophenylene-*N*-imide of maleopimaric acid **V** and 1 mmol of substituted benzaldehydes of vanillin series **VI**, 10 ml of anhydrous methanol and 10 ml of anhydrous DMF was refluxed for 3–4 h. The reaction mixture was diluted with 50–60 ml of water. The precipitated product was filtered off on a glass porous filter, washed with water and cold methanol, dried in air for 5–6 h at 40–50°C.

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