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Synthesis of Azomethines by Condensation of Substituted Benzaldehydes with 3-Aminophenylen-*N*-imide of Maleopimaric Acid

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

[a] *Institute of Chemistry of New Materials, Belarus National Academy of Sciences, Minsk, Belarus*
[b] *Institute of Physical Organic Chemistry, Belarus National Academy of Sciences, ul. Surganova 13, Minsk, 220072, Belarus*
e-mail: dikusar@ifoch.bas-net.by

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Abstract—New method for the synthesis of azomethines by condensation of substituted benzaldehydes of the vanillin series with 3-aminophenylen-*N*-imide of maleopimaric acid is developed.

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We have reported previously on the synthesis of aromatic azomethines prepared by condensation of substituted benzaldehydes of vanillin series **VI** with 4-aminophenylen-*N*-imide of maleopimaric acid [1].

In this paper the synthesis of new azomethines by means of condensation of substituted benzaldehydes with 3-aminophenylen-*N*-imide of maleopimaric acid **V** is described.

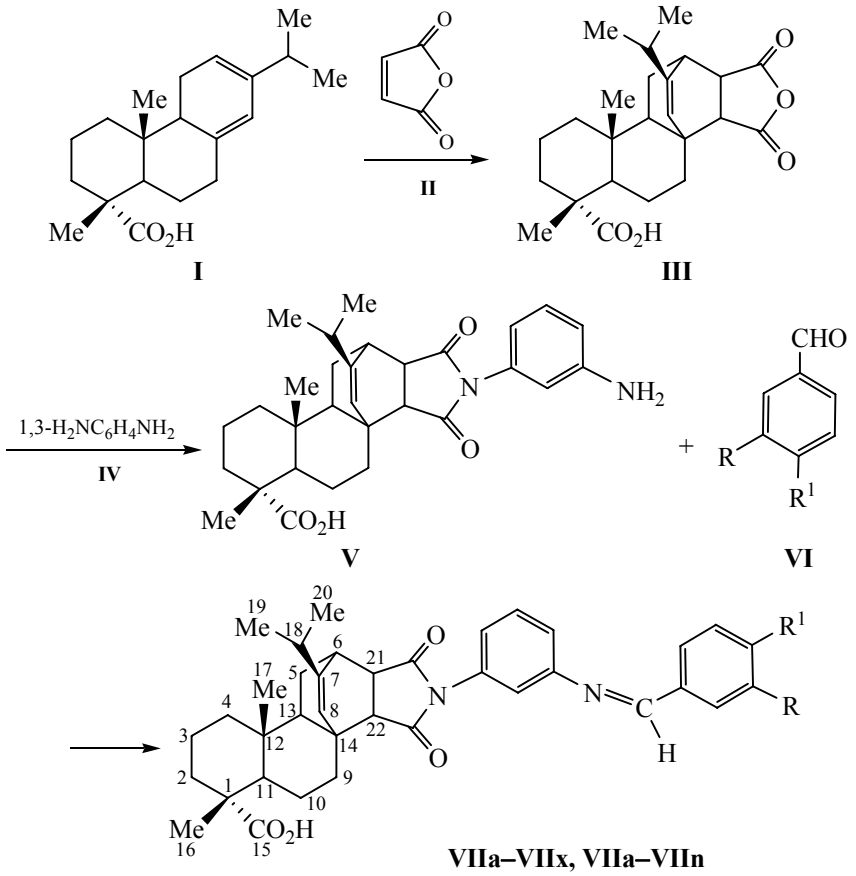
We managed to involve 3-aminophenylen-*N*-imide of maleopimaric acid **V** in the condensation with substituted benzaldehydes of vanillin series **VI** to form azomethines containing the fragment of maleopimaric acid (**VIIa–VIIx**, **VIIIa–VIIIn**), ether and ester groups (**VIIb–VIIx**, **VIIIb–VIIIn**), adamantane fragments (**VIIv**, **VIIIl**), *o*- and *m*-carboranes (**IIIw, IIIx**, **IVm, IVn**).

The condensation was carried out by boiling the mixture of starting compounds **V** and **VI** in the 1:1 molar ratio in a 1:1 mixture of anhydrous methanol and DMSO for 3–4 h. Yields of azomethines **VIIa–VIIx, VIIIa–VIIIn** were 71–85%.

The azomethines **IIIa–IIIx, IVa–IVn** synthesized are crystalline compounds soluble in DMF and DMSO and poorly soluble in methanol, diethyl ether, chloroform, and hydrocarbons. The structure of azomethines **IIIa–IIIx, IVa–IVn** was established from the IR and ^{1}H NMR spectra, and their composition was confirmed by the elemental analysis data (see the table). The purity of the compound obtained according to ^{1}H NMR data was 92±1%.

In the IR spectra of azomethines **IIIa–IIIx, IVa–IVn** the following characteristic absorption bands were observed (ν, cm^{-1}): OH_{acidic} 2200–3600, CH_{arom} 3080–3005, 870–650, CH_{aliph} 2995–2830, C–O 1780–1620, C=N 1630–1625, $C=C_{arom}$ 1600±5, 1515±2, 1388±2, CO 1290–1000. In the IR spectrum of compound **IIIs** the presence of NO_2 group was confirmed by the characteristic absorption bands in the range 1534 and 1351 cm^{-1}. In the IR spectra of carborane-containing azomethines **IIIw, IIIx, IVm, IVn** CH_{carb} absorption bands at 3070 (**IIIw, IVm**) and 3034 (**IIIx, IVn**) are present, and the BH vibration is observed at 2680–2658 cm^{-1}.

In the ^{1}H NMR spectra of azomethines **IIIa–IIIx, IVa–IVn** the signals of protons of the maleopimaric acid fragment appear in the range (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), 9.70–10.10 br.s (1H, COOH). In the ^{1}H NMR spectra of azomethines **IIIb–IIIx**, **IVb, VIa** the signals of the MeO group protons are observed as a singlet in the range 3.85–3.90 ppm, and in the spectra of compounds **IVa–IVn, VIb** signals of the EtO group give rise to a triplet in the range 0.90–1.30 ppm (Me) and a quartet at 3.80–4.20 ppm (CH_2). The signals of aromatic protons in the compounds **IIIa–IIIx, IVa–IVn**, **V, VIa, VIb** are located in the range 6.60–7.90 ppm, and



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**).

the protons of azomethine group HC=N give a singlet at 8.44–8.50 ppm characteristic of azomethines with *E*-configuration [2].

In the IR and ^{1}H NMR spectra of azomethines I**IIa–IIIx, IVa–IVn** the absorption bands and the signals of protons confirming the presence of the corresponding structural fragments of the ester groups are present [3].

EXPERIMENTAL

IR spectra of the compounds obtained were recorded on a Nicolet Protégé-460 IR Fourier spectrometer in thin layer or in KBr pellets. ^{1}H NMR spectra were taken on a Tesla BS-587A (100 MHz) spectrometer from 5% solutions in DMSO-d_6. Chemical shifts were presented with respect to TMS. Elemental analysis was carried out on an Elemental Vario EL-III C,H,N,O,S-analyzer. Evaluation error was 0.1%.

Vanillin and vanillal esters **VI** were synthesized according to procedures [4–9].

Maleopimaric acid 3-aminophenylen-*N*-imide (V) was synthesized according to the modified procedure [10]. A solution of 25 mmol of maleopimaric acid **III** and 25 mmol of 1,3-phenylenediamine **IV** in 60 ml of pyridine was refluxed for 5 h. After the reaction was complete pyridine was distilled off, and the solid residue obtained was washed on a filter with 300 ml of hot water (70–100°C) and dried in air. Maleopimaric acid 3-aminophenylen-*N*-imide **V**, 12.1 g (99%), was

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

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VIIa	85	213–214	77.19	7.48	4.50	$C_{37}H_{42}N_2O_4$	76.79	7.31	4.84
VIIb	84	162–163	75.22	7.29	4.32	$C_{38}H_{44}N_2O_5$	74.97	7.29	4.60
VIIc	78	235–236	73.31	7.31	4.23	$C_{38}H_{44}N_2O_6$	73.05	7.10	4.48
VIId	84	238–239	73.58	7.27	3.87	$C_{39}H_{46}N_2O_6$	73.33	7.26	4.39
VIIe	88	228–229	72.32	6.84	3.88	$C_{40}H_{46}N_2O_7$	72.02	6.95	4.20
VIIf	86	162–163	72.19	7.32	3.80	$C_{41}H_{48}N_2O_7$	72.33	7.11	4.11
VIIg	71	146–147	72.25	7.31	3.61	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIh	85	127–128	72.65	7.19	4.78	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIi	86	104–105	73.37	7.38	3.43	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIj	83	113–114	72.90	7.25	3.81	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIk	85	117–118	73.61	7.61	3.32	$C_{46}H_{58}N_2O_7$	73.57	7.78	3.73
VIIl	82	111–112	74.34	8.22	3.17	$C_{48}H_{62}N_2O_7$	74.01	8.02	3.60
VIIm	82	55–56	75.76	8.80	2.60	$C_{56}H_{78}N_2O_7$	75.47	8.82	3.14
VIIn	83	128–129	73.32	7.14	3.70	$C_{42}H_{48}N_2O_7$	72.81	6.98	4.04
VIIo	85	97–98	75.16	7.23	3.37	$C_{48}H_{54}N_2O_7$	74.78	7.06	3.63
VIIp	80	134–135	74.34	6.47	3.44	$C_{45}H_{48}N_2O_7$	74.15	6.64	3.84
VIIq[a]	72	121–122	67.86	5.76	3.04	$C_{45}H_{46}Cl_2N_2O_7$	67.75	5.81	3.51
VIIr[b]	82	132–133	67.30	5.78	3.13	$C_{45}H_{47}BrN_2O_7$	66.91	5.86	3.47
VIIs	85	138–139	70.14	6.10	5.01	$C_{45}H_{47}N_3O_9$	69.84	6.12	5.43
VIIt	83	187–188	70.84	6.84	3.54	$C_{40}H_{46}N_2O_8$	70.36	6.79	4.10
VIIu	83	182–183	71.03	6.81	3.82	$C_{41}H_{48}N_2O_8$	70.67	6.94	4.02
VIIv	80	159–160	75.14	7.43	3.56	$C_{49}H_{58}N_2O_7$	74.78	7.43	3.56
VIIw[c]	83	261–262	62.25	6.85	3.14	$C_{41}H_{54}B_{10}N_2O_7$	61.94	6.85	3.52
VIIx[d]	84	277–278	62.22	7.01	3.22	$C_{41}H_{54}B_{10}N_2O_7$	61.94	6.85	3.52
VIIIa	79	222–223	73.43	7.24	4.08	$C_{39}H_{46}N_2O_6$	73.33	7.26	4.39
VIIIb	80	221–222	73.65	7.62	3.90	$C_{40}H_{48}N_2O_6$	73.59	7.41	4.29
VIIIc	82	192–193	72.51	7.30	3.83	$C_{41}H_{48}N_2O_7$	72.33	7.11	4.11
VIIId	83	105–106	73.12	7.52	3.82	$C_{42}H_{50}N_2O_7$	72.60	7.25	4.03
VIIIe	85	117–118	73.13	7.53	3.48	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIIf	84	102–103	72.81	7.43	3.63	$C_{43}H_{52}N_2O_7$	72.86	7.39	3.95
VIIIg	85	125–126	73.43	7.57	3.60	$C_{44}H_{54}N_2O_7$	73.10	7.53	3.88
VIIIh	81	103–104	73.56	7.40	3.34	$C_{44}H_{54}N_2O_7$	73.10	7.53	3.88
VIIIi	72	125–126	74.92	7.06	3.27	$C_{47}H_{52}N_2O_7$	74.58	6.92	3.70
VIIIj	80	196–197	70.80	7.12	3.85	$C_{41}H_{48}N_2O_8$	70.67	6.94	4.02
VIIIk	81	127–128	71.34	7.22	3.43	$C_{42}H_{50}N_2O_8$	70.96	7.09	3.94
VIIIl	82	181–182	75.18	7.38	3.38	$C_{50}H_{60}N_2O_7$	74.97	7.55	3.50
VIIIm[e]	80	238–239	62.65	6.99	3.32	$C_{42}H_{56}B_{10}N_2O_7$	62.35	6.98	3.46
VIIIn[f]	82	220–221	62.40	7.10	3.28	$C_{42}H_{56}B_{10}N_2O_7$	62.35	6.98	3.46

[a] Found Cl,%: 8.63, calculated Cl,%: 8.89. [b] Found Br,%: (.48. Calculated Br,%: 9.89. [c] Found B,%: 13.25. Calculated B,%: 13.60. [d] Found B,%: 13.29. Calculated B,%: 13.60. [e] ound B,%: 12.91. Calculated B,%: 13.35. [f] Found B,%: 13.04. Calculated B,%: 13.36.

obtained, mp 278–279°C. IR spectrum (KBr), ν, cm^{-1}: 2550–2600 (OH); 1770, 1700 [(C=O)N]; 1510 ($C=C_{arom}$). ^1H NMR spectrum (DMF-d_7), δ, ppm: 0.63 s (3H, $C^{17}H_3$); 0.95 m (1H); 0.96 d, 0.98 d [6H, $(CH_3)_2CH$, *J* 7 Hz]; 1.12 s (3H, $C^{16}H_3$); 1.22–1.30 m (2H); 1.41–1.34 m (10H); 2.20 sextet [1H, $(CH_3)_2CH$]; 2.51 m (1H, C^9H_{eq}); 2.71 d (1H, $C^{22}H$, *J* 7.5 Hz); 3.01 br.s (1H, C^6H); 3.07 m (1H, $C^{21}H$); 5.60 d (1H, C^8H, *J* 7 Hz); 7.34 m (2H, H_{arom}), 7.80 m (1H, H_{arom}), 8.59 m (1H, H_{arom}).

Functionalyzed aromatic azomethines VIIa–VIIx, VIIIa–VIIIn. A mixture of 1 mmol of maleopimaric acid 3-aminophenylen-*N*-imide **V** and 1 mmol of substituted benzaldehyde of vanillal series **VI**, 10 ml of anhydrous methanol and 10 ml of anhydrous DMSO was refluxed for 3–4 h. After that the reaction mixture was diluted with 50–60 ml of water, and the product formed was filtered off on a glass frit filter, washed with water and cold methanol, and dried in air for 5–6 h at 40–50°C.

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