

SHORT
COMMUNICATIONSDerivatives of α,β -Dehydro Amino Acids. Synthesis of 2-Aryl-4-arylmethylidene-1-arylmethylideneamino-4,5-dihydro-1*H*-imidazol-5-ones by Reaction of *N*-Substituted α,β -Dehydro Amino Acid Arylmethylidenehydrazides with HexamethyldisilazaneV. O. Topuzyan^a, L. G. Arutyunyan^a, A. A. Oganesyan^a, and G. A. Panosyan^b^a Institute of Fine Organic Chemistry, National Academy of Sciences of Armenia,
pr. Azatutyana 26, Erevan, 375014 Armenia
e-mail: vtop@web.am^b Molecular Structure Research Center, National Academy of Sciences of Armenia, Erevan, Armenia

Received May 4, 2006

DOI: 10.1134/S1070428008030299

The synthesis of 4-arylmethylidene-1-(arylmethylideneamino)imidazol-5-ones via cyclization of *N*-benzoyl α,β -dehydro amino acid arylmethylidenehydrazides by the action of acid reagents was reported in [1, 2]. We recently showed that primary amides [3], arylamides [4], and hydrazides derived from *N*-substituted α,β -dehydro amino acids [5] in the presence of silylating agents (chlorotrimethylsilane, hexamethyldisilazane) undergo dehydration to give 2,4-di- or 1,2,4-trisubstituted imidazol-5-ones.

In the present communication we describe the synthesis of 2-aryl-4-arylmethylidene-1-arylmethylideneamino-4,5-dihydro-1*H*-imidazol-5-ones **II** by cyclization of *N*-substituted α,β -unsaturated amino acid arylmethylidenehydrazides **I** in the presence of hexamethyldisilazane (HMDS). The reactions were carried out by heating the reactants in boiling DMF for 15–30 min. The proposed procedure for the cyclization of com-

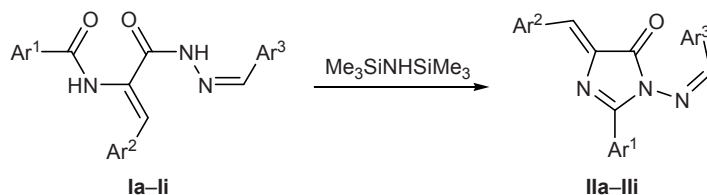
pounds **I** is more advantageous than those reported in [1, 2] from the viewpoints of both reaction time and yield of the target imidazol-5-ones.

The ¹H NMR spectra of compounds **IIa–III** contained a singlet from the CH=C proton at δ 7.07–7.22 ppm, indicating their *Z* configuration (cf. [2]).

N-[2-(4-Methoxyphenyl)-1-(3,4-methylenedioxybenzylidenehydrazinocarbonyl)ethenyl]benzamide (**Ie**). Yield 78%, mp 212–214°C. Found, %: C 67.59; H 4.91; N 9.13. C₂₅H₂₁N₃O₅. Calculated, %: C 67.71; H 4.77; N 9.47.

N-[1-(4-Methoxybenzylidenehydrazinocarbonyl)-2-(3,4-methylenedioxyphenyl)ethenyl]furan-2-carboxamide (**Ig**). Yield 92%, mp 225–226°C. Found, %: C 64.00; H 4.61; N 9.43. C₂₃H₁₉N₃O₆. Calculated, %: C 63.74; H 4.42; N 9.69.

N-[2-(3,4-Methylenedioxyphenyl)-1-(3-nitrobenzylidenehydrazinocarbonyl)ethenyl]furan-2-car-



I, **II**, $\text{Ar}^1 = \text{Ar}^2 = \text{Ar}^3 = \text{Ph}$ (**a**); $\text{Ar}^1 = \text{Ar}^2 = \text{Ph}$, $\text{Ar}^3 = 4\text{-MeOC}_6\text{H}_4$ (**b**); $\text{Ar}^1 = \text{Ar}^3 = \text{Ph}$, $\text{Ar}^2 = 4\text{-MeOC}_6\text{H}_4$ (**c**); $\text{Ar}^1 = \text{Ph}$, $\text{Ar}^2 = \text{Ar}^3 = 4\text{-MeOC}_6\text{H}_4$ (**d**); $\text{Ar}^1 = \text{Ph}$, $\text{Ar}^2 = 4\text{-MeOC}_6\text{H}_4$, $\text{Ar}^3 = 3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$ (**e**); $\text{Ar}^1 = \text{Ar}^3 = \text{Ph}$, $\text{Ar}^2 = 3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$ (**f**); $\text{Ar}^1 = 2\text{-furyl}$, $\text{Ar}^2 = 3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$, $\text{Ar}^3 = 4\text{-MeOC}_6\text{H}_4$ (**g**); $\text{Ar}^1 = 2\text{-furyl}$, $\text{Ar}^2 = 3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$, $\text{Ar}^3 = 3\text{-O}_2\text{NC}_6\text{H}_4$ (**h**); $\text{Ar}^1 = 2\text{-furyl}$, $\text{Ar}^2 = 3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$, $\text{Ar}^3 = \text{PhCH}=\text{CH}$ (**i**).

boxamide (Ih). Yield 91%, mp 235–238°C. Found, %: C 59.09; H 3.82; N 12.16. $C_{22}H_{16}N_4O_7$. Calculated, %: C 58.93; H 3.59; N 12.49.

***N*-[2-(3,4-Methylenedioxyphenyl)-1-(3-phenylprop-2-en-1-ylidenehydrazinocarbonyl)ethenyl]-furan-2-carboxamide (Ii).** Yield 90%, mp 194–196°C. Found, %: C 67.48; H 4.76; N 9.55. $C_{24}H_{19}N_3O_5$. Calculated, %: C 67.13; H 4.56; N 9.78.

2-Aryl-4-arylmethylidene-1-arylmethylidene-amino-4,5-dihydro-1H-imidazol-5-ones IIa–III (general procedure). Hexamethyldisilazane, 1 ml (0.03 mol), was added to a solution of 0.01 mol of compound Ia–Ii in 10 ml of DMF, and the mixture was heated for 15–30 min under reflux (the mixture turned brown). The mixture was cooled to room temperature and diluted with 70 ml of water, and the yellow precipitate was filtered off and recrystallized from ethanol or ethanol–benzene (1 : 1).

4-Benzylidene-1-benzylideneamino-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IIa). Reaction time 15 min; yield 85%, mp 189–192°C; published data [3]: mp 181–183°C; R_f 0.81. IR spectrum, ν , cm^{-1} : 1705, 1640. 1H NMR spectrum, δ , ppm: 7.22 s (1H, C=CH), 7.36–7.64 m (9H, H_{arom}), 7.81 m (2H, H_{arom}), 8.22–8.34 m (4H, H_{arom}), 9.59 s (1H, N=CH). Found, %: N 12.08. $C_{23}H_{17}N_3O$. Calculated, %: N 11.96.

4-Benzylidene-1-(4-methoxybenzylideneamino)-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IIb). Reaction time 30 min; yield 84%, mp 168–170°C, R_f 0.81. IR spectrum, ν , cm^{-1} : 1702, 1635. 1H NMR spectrum, δ , ppm: 3.86 s (3H, OCH₃), 6.97 m (2H, H_{arom}), 7.19 s (1H, C=CH), 7.36–7.62 m (6H, H_{arom}), 7.74 m (2H, H_{arom}), 8.27 m (4H, H_{arom}), 9.45 s (1H, N=CH). Found, %: N 11.19. $C_{24}H_{19}N_3O_2$. Calculated, %: N 11.02.

1-Benzylideneamino-4-(4-methoxybenzylidene)-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IIc). Reaction time 30 min; yield 82%, mp 192–194°C; published data [4]: mp 178–182°C; R_f 0.83. IR spectrum, ν , cm^{-1} : 1700, 1635.3. 1H NMR spectrum, δ , ppm: 3.88 s (3H, OCH₃), 6.97 m (2H, H_{arom}), 7.19 s (1H, C=CH), 7.41–7.61 m (6H, H_{arom}), 7.80 m (2H, H_{arom}), 8.23 m (2H, H_{arom}), 8.28 m (2H, H_{arom}), 9.61 s (1H, N=CH). Found, %: N 11.13. $C_{24}H_{19}N_3O_2$. Calculated, %: N 11.03.

4-(4-Methoxybenzylidene)-1-(4-methoxybenzylideneamino)-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IId). Reaction time 30 min; yield 84%, mp 198–200°C; published data [4]: mp 185–189°C; R_f 0.80. IR spectrum, ν , cm^{-1} : 1710, 1630. 1H NMR

spectrum, δ , ppm: 3.87 s (3H, OCH₃), 3.88 s (3H, OCH₃), 6.98 m (4H, H_{arom}), 7.16 s (1H, C=CH), 7.47–7.60 m (3H, H_{arom}), 7.74 m (2H, H_{arom}), 8.23 m (2H, H_{arom}), 8.28 m (2H, H_{arom}), 9.47 s (1H, N=CH). Found, %: N 10.00. $C_{25}H_{21}N_3O_3$. Calculated, %: N 10.21.

4-(4-Methoxybenzylidene)-1-(3,4-methylenedioxybenzylideneamino)-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IIe). Reaction time 30 min, yield 83%, mp 247–250°C, R_f 0.78. IR spectrum, ν , cm^{-1} : 1700, 1635. 1H NMR spectrum, δ , ppm: 3.88 s (3H, OCH₃), 6.07 s (2H, OCH₂O), 6.90 d (1H, C₆H₃, J = 7.93 Hz), 6.99 m (2H, C₆H₄), 7.16 s (1H, C=CH), 7.26 d.d (1H, C₆H₃, J = 1.83, 7.93 Hz), 7.31 d (1H, C₆H₃, J = 1.60 Hz), 7.47–7.60 m (3H, H_{arom}), 8.21 m (2H, H_{arom}), 8.27 m (2H, H_{arom}), 9.44 s (1H, N=CH). Found, %: N 10.07. $C_{23}H_{17}N_3O$. Calculated, %: N 9.87.

1-Benzylideneamino-4-(3,4-methylenedioxybenzylidene)-2-phenyl-4,5-dihydro-1H-imidazol-5-one (IIf). Reaction time 20 min, yield 71%, mp 237–240°C, R_f 0.90. IR spectrum, ν , cm^{-1} : 1695, 1645. 1H NMR spectrum, δ , ppm: 6.09 s (2H, OCH₂O), 6.90 d (1H, C₆H₃, J = 7.91 Hz), 7.14 s (1H, C=CH), 7.40–7.64 m (6H, H_{arom}), 7.60 d (1H, C₆H₃, J = 1.13, 7.98 Hz), 7.80 m (2H, H_{arom}), 8.17 d (1H, C₆H₃, J = 1.08 Hz), 8.22 m (2H, C₆H₅), 9.59 s (1H, N=CH). Found, %: N 10.51. $C_{24}H_{17}N_3O_3$. Calculated, %: N 10.63.

2-(2-Furyl)-1-(4-methoxybenzylideneamino)-4-(3,4-methylenedioxybenzylidene)-4,5-dihydro-1H-imidazol-5-one (IIg). Reaction time 15 min, yield 88%, mp 278–280°C, R_f 0.80. IR spectrum, ν , cm^{-1} : 1700, 1630. 1H NMR spectrum, δ , ppm: 3.88 s (3H, OCH₃), 6.10 s (2H, OCH₂O), 6.71 d.d (1H, Fu, J = 1.76, 3.55 Hz), 6.92 d (1H, C₆H₃, J = 8.07 Hz), 7.02 m (2H, C₆H₄), 7.08 s (1H, C=CH), 7.57 d.d (1H, C₆H₃, J = 1.75, 8.10 Hz), 7.58 d (1H, Fu, J = 3.61 Hz), 7.80 m (2H, C₆H₄), 7.98 d (1H, Fu, J = 1.78 Hz), 8.18 d (1H, C₆H₃, J = 1.72 Hz), 9.51 s (1H, N=CH). Found, %: N 10.28. $C_{23}H_{17}N_3O_5$. Calculated, %: N 10.11.

2-(2-Furyl)-4-(3,4-methylenedioxybenzylidene)-1-(3-nitrobenzylideneamino)-4,5-dihydro-1H-imidazol-5-one (IIh). Reaction time 15 min, yield 96%, mp 294–297°C, R_f 0.76. IR spectrum, ν , cm^{-1} : 1715, 1625. 1H NMR spectrum, δ , ppm: 6.11 s (2H, OCH₂O), 6.76 d.d (1H, Fu, J = 1.82, 3.57 Hz), 6.94 d (1H, C₆H₃, J = 8.17 Hz), 7.16 s (1H, C=CH), 7.58 d (1H, Fu, J = 3.57 Hz), 7.61 d.d (1H, C₆H₃, J = 1.79, 8.26 Hz), 7.81 t (1H, C₆H₄, J = 8.05 Hz), 8.03 d (1H, Fu, J = 1.94 Hz), 8.18 d (1H, C₆H₃, J = 1.71 Hz), 8.32 d.d (1H, C₆H₄, J = 1.81, 7.96 Hz), 8.35 d.d (1H, C₆H₄, J = 2.04,

7.96 Hz), 8.69 t (1H, C₆H₄, *J* = 1.98 Hz), 9.84 s (1H, N=CH). Found, %: N 12.93. C₂₂H₁₄N₄O₆. Calculated, %: N 13.02.

2-(2-Furyl)-4-(3,4-methylenedioxybenzylidene)-1-(3-phenylprop-2-en-1-ylideneamino)-4,5-dihydro-1H-imidazol-5-one (III). Reaction time 30 min, yield 74%, mp 269–271°C, *R*_f 0.78. IR spectrum, ν , cm⁻¹: 1695, 1630. ¹H NMR spectrum, δ , ppm: 6.09 s (2H, OCH₂O), 6.68 d.d (1H, Fu, *J* = 1.75, 3.53 Hz), 6.90 d (1H, C₆H₃, *J* = 8.18 Hz), 7.05 d.d (1H, CH=C, *J* = 9.17, 15.87 Hz), 7.07 s (1H, C=CH), 7.26 d (1H, CH=C, *J* = 15.94 Hz), 7.29–7.43 m (3H, H_{arom}), 7.55 d.d (1H, C₆H₃, *J* = 1.73, 8.25 Hz), 7.60 m (2H, H_{arom}), 7.66 d (1H, Fu, *J* = 3.57 Hz), 7.94 d (1H, Fu, *J* = 2.01 Hz), 8.18 d (1H, C₆H₃, *J* = 1.67 Hz), 9.48 s (1H, N=CH). Found, %: N 10.03. C₂₄H₁₇N₃O₄. Calculated, %: N 10.21.

The IR spectra were recorded on a Specord M-80 spectrometer. The ¹H NMR spectra were measured on a Varian Mercury 300 instrument from solutions in

DMSO-*d*₆. The purity of the products was checked by TLC on Silufol UV-254 plates using toluene–hexane–ethanol (1:1:1) as eluent; spots were detected under UV light or by treatment with iodine vapor. Initial compounds **Ia–Ii** were synthesized according to the procedure described in [2].

REFERENCES

1. Budovskii, E.I., Khamutov, R.M., Karpenskii, M.Ya., Severin, E.S., and Kochetkov, N.K., *Zh. Obshch. Khim.*, 1960, vol. 30, p. 2569.
2. Nalepa, K., Zednikova, G., Marek, J., and Travnicek, Z., *Monatsh. Chem.*, 1999, vol. 130, p. 471.
3. Topuzyan, V.O., Arutyunyan, L.G., and Oganessian, A.A., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 868.
4. Topuzyan, V.O., Oganessian, A.A., and Panosyan, G.A., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1644.
5. Topuzyan, V.O., Arutyunyan, L.G., Oganessian, A.A., and Panosyan, G.A., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 936.