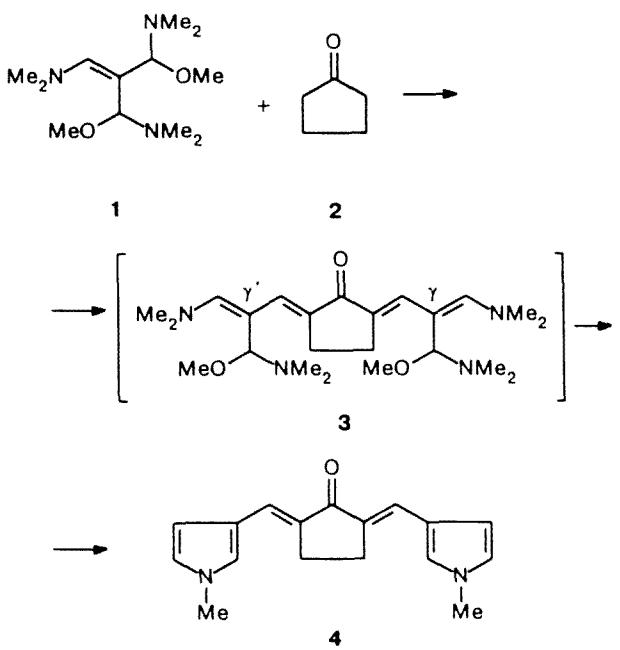
A novel route of pyrrole ring formation

Zh. A. Krasnaya, Yu. V. Smirnova, and V. S. Bogdanov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117334 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: L112@suearn2.bitnet

We expected that the condensation of β-dimethylaminomethylenemalonaldehyde bis-*N,O*-acetal[1] (**1**) with cyclopentanone (**2**) in a ratio of 2 : 1 would result in the formation of polyenic bis-dimethylaminoketone (**3**), containing *N,O*-acetal groups at g,γ′-positions. However, previously unknown β,β′-bis(*N*-methylpyrrolyl-3)divinylketone (**4**) was unexpectedly formed in a yield of 13 % instead of ketone **3**. It is likely that compound **4** was formed due to intramolecular cyclization of ketone **3** involving one of the methyl groups of the dimethylamino group and the *N,O*-acetal function (Scheme 1).

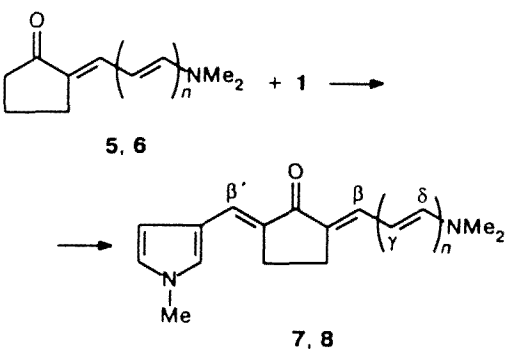
Scheme 1



The reaction of compound **1** with conjugated dimethylaminoketones **5** and **6** at an equimolar ratio of the reagents occurs similarly to form previously unknown unsaturated aminoketones **7** and **8**, containing the *N*-methylpyrrole cycle at the β′-position, in yields of 40 and 44 %, respectively (Scheme 2).

The condensation was performed at 75 to 100 °C for 0.5 to 2 h. In some cases, the reaction mass formed

Scheme 2



5, **7**: $n = 0$
6, **8**: $n = 1$

was diluted with methylene chloride, silica gel was added, and the mass was kept for 1 day at ~20 °C. The structures of compounds **4**, **7**, and **8** were confirmed by the data of ^{1}H NMR, UV, and mass spectra. The signals of protons in the *N*-methylpyrrole cycle were assigned according to the literature data[2] for *N*-methyl-3-phenylpyrrole.

2,5-Bis(*N*-methylpyrrolyl-3)methylenecyclopentanone (4). Product **4** (60 mg, 13 %) was obtained from compounds **2** (0.15 mL) and **1** (0.92 g) as red crystals with m.p. (decomp.) 239—243 °C. UV (EtOH), λ_{max}/nm: 420 (56550), 405 sh (46700). ^{1}H NMR (CD_2Cl_2), δ: 2.90 (s, 4 H, CH_2); 3.70 (s, 6 H, NMe); 6.40 (br.s, 2 H, H-4, pyrrolyl); 6.69 (br.s, 2 H, H-5, pyrrolyl); 6.96 (br.s, 2 H, H-2, pyrrolyl); 7.39 (s, 2 H, C=C<u>H</u>). Mass spectrum, *m/z*: 266 [M^+].

2-Dimethylaminomethylene-5-(*N*-methylpyrrolyl-3′)methylenecyclopentanone (7) was obtained in a yield of 40 % (190 mg) from compounds **1** (0.6 g) and **5** (0.3 g) as yellow-brown crystals with m.p. (decomp.) 213—215 °C. Found (%): C, 72.88; H, 8.01; N, 11.95. $C_{14}H_{18}N_2O$. Calculated (%): C, 73.00; H, 7.88; N, 12.16. UV (EtOH), λ_{max}/nm: 405 (54100), 416 sh (46060). ^{1}H NMR (CD_2Cl_2), δ: 2.61 (m, 2 H, CH_2); 2.99 (m, 2 H, CH_2); 3.10 (s, 6 H, NMe_2); 3.66 (s, 3 H, NMe); 6.32 (t, 1 H, H-4, pyrrolyl, $J_{4,5}$ = 2.5 Hz); 6.62 (t, 1 H, H-5, pyrrolyl, $J_{4,5} = J_{2,5}$ = 2.5 Hz); 6.84 (t, 1 H, H_β, J_{β,CH_2} = 1.7 Hz); 7.12 (t, 1 H, H-2, pyrrolyl,

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 785—786, March, 1996.

1066-5285/96/4503-0745 $15.00

$J_{2,5}$ = 2.5 Hz); 7.26 (t, 1 H, $H_{\beta'}$, J_{β',CH_2} = 1.7 Hz). Mass spectrum, *m/z*: 230 [M^+].

2-(3-Dimethylaminopropen-2′-ylidene)-5-(*N*-methylpyrrolyl-3′)methylenecyclopentanone (8) was obtained in a yield of 44 % (170 mg) from compounds **6** (0.25 g) and **1** (0.41 g) as red crystals with m.p. (decomp.) >210 °C. Found (%): N, 10.43. $C_{16}H_{20}N_2O$. Calculated (%): N, 10.93. UV (EtOH), λ_{max}/nm: 474 (117700). ^{1}H NMR (CD_2Cl_2), δ: 2.68 (m, 2 H, CH_2); 2.79 (m, 2 H, CH_2); 2.91 (s, 6 H, NMe_2); 3.68 (s, 3 H, NMe); 5.03 (t, 1 H, H_γ, $J_{\gamma,\delta}$ = $J_{\beta,\gamma}$ = 12.5 Hz); 6.34 (t, 1 H, H-4, pyrrolyl, $J_{4,5}$ = 2.5 Hz); 6.63 (t, 1 H, H-5, pyrrolyl, $J_{4,5}$ = $J_{2,5}$ = 2.5 Hz); 6.80 (d, 1 H, H_δ, $J_{\gamma,\delta}$ = 12.5 Hz); 6.90 (t, 1 H, $H_{\beta'}$, J_{β',CH_2} = 2.5 Hz); 7.14 (d, 1 H, H_β, $J_{\beta,\gamma}$ = 12.5 Hz); 7.20 (t, 1 H, H-2, pyrrolyl, $J_{2,5}$ = 2.5 Hz). Mass spectrum, *m/z*: 256 [M^+].

References

1. Zh. A. Krasnaya, Yu. V. Smirnova, G. V. Krystal, and V. S. Bogdanov, *Mendeleev Commun.*, 1996, 17.
2. Zh. A. Krasnaya and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1064 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 771 (Engl. Transl.)].

Received December 20, 1995