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Aminaleacetal of dimethylaminomethylenemalonaldehyde – a novel reagent for the synthesis of substituted aminopolyenes

Zhanna A. Krasnaya,* Yuliya V. Smirnova, Galina V. Krystal and Valentin S. Bogdanov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 5328

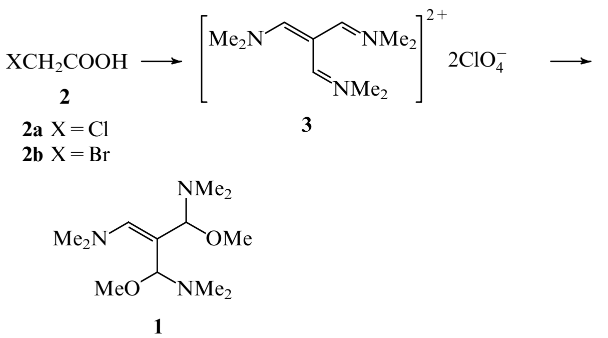
Synthesis of the previously unknown bis-aminaleacetal of dimethylaminomethylenemalonaldehyde has been developed, condensation of which with malonates affords trienic δ-dimethylaminotetraesters.

As shown previously, aminals and aminaleacetals of conjugated β-dimethylaminoaldehydes $Me_2N(CH{=}CH)_nCH(Y)NMe_2$ (n = 1–4, Y = OMe, NMe_2) are convenient reagents for the synthesis of various types of aminopolyenes, because they condense easily with ketones, β-diketones and CH-acids, on reactive methyl and methylene groups, without the need for catalysts.[1–4]

Investigations of aminopolyenes have shown that they possess a number of specific properties, *viz.* solvatochromism, thermochromism, fluorescence, laser-emitted light generation, *etc.*[5–7]

In this work a method of synthesizing the previously unknown bis-aminaleacetal of dimethylaminomethylenemalonaldehyde has been developed, with the aim of obtaining new types of substituted aminopolyenes. Bis-aminaleacetal **1** was prepared from bis-perchlorate **3** (Scheme 1).[†]

The synthesis of starting compound **3** has been described earlier.[8] However, our attempts to obtain bis-perchlorate **3** by formylation of chloroacetic acid **2a** according to this procedure[8] were unsuccessful. Only inorganic salts were isolated from the reaction mixture following the recommended treatment with ice and a concentrated aqueous solution of $NaClO_4$.

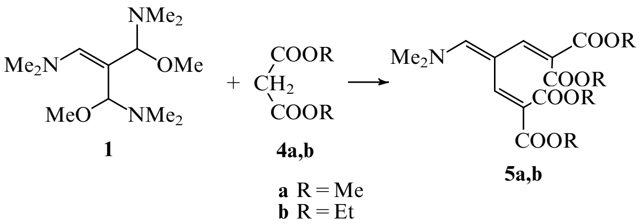


Scheme 1

Bis-perchlorate **3** was, however, prepared after changing the order of adding the reagents [$POCl_3$ was added dropwise to a solution of **2a** in absolute dimethylformamide (DMF)] and on treatment of the reaction solution with EtOH, H_2O and 35% aqueous $HClO_4$. The yield of bis-perchlorate **3**, however, was not greater than 25%.

Formylation of bromoacetic acid **2b** as above allowed us to increase the yield of salt **3** (up to 76%).

Bis-aminaleacetal **1** was prepared by interaction of bis-perchlorate **3** with MeOK in benzene solution in the presence of $NHMe_2$. From ^1H NMR spectral data compound **1** was shown to be bis-aminaleacetal (NMe_2 and OMe group ratio 1:1). The arrangement of NMe_2 and OMe (Scheme 1) is conditional, since OMe groups can be located on one carbon atom, while NMe_2 groups are also on another. Following



Scheme 2

[†] *Compound* **3**. To a stirred mixture of **2b** (20.8 g, 0.15 mol) in dry DMF (65 ml) was added dropwise $POCl_3$ (49 ml, 0.54 mol) over 3 h at 5–12 °C. The mixture was heated slowly and stirred at 90 °C for 10 h. The reaction solution was then cooled to −20 to −25 °C and treated dropwise with EtOH (60 ml), H_2O (120 ml) and 35% aqueous $HClO_4$ (70 ml) with stirring. The temperature of the reaction mixture was kept at −20 to −25 °C for 2 h; the resulting solid was filtered off, washed with EtOH and dried under reduced pressure over $CaCl_2$ at room temperature to give 43.7 g (76%) of bis-perchlorate **3**. Characteristic data for compound **3** are given in ref. 8.

Compound **1**. To a stirred suspension of MeOK in dry benzene, that had been obtained from K (4.9 g, 0.13 mol) and dry MeOH (5.3 ml, 0.13 mol) in a nitrogen atmosphere at 6 °C was added bis-perchlorate **3** (12 g, 0.03 mol) and a solution of Me_2NH in dry benzene (1:1, 12 ml). The mixture was then heated rapidly to 25 °C and stirred for 1 h. The resulting solution was filtered, solids washed extensively with dry C_6H_6 and the solvent removed under reduced pressure. The oil was distilled *in vacuo* to give 5 g (60%) of bis-aminaleacetal of dimethylaminomethylenemalonaldehyde **1**, bp 68–70 °C (0.6 mmHg); n_D^{20} 1.4788; ^1H NMR (C_6D_6): 6.12 and 6.20 (1H, CH=), 4.50, 4.42 and 4.28 (2H, CH), 3.25–3.38 (6H, m, OMe), 2.75 (6H, m, NMe_2), 2.46–2.56 (12H, m, NMe_2).

distillation *in vacuo* (0.6 mmHg), bis-aminaleacetal **1** was found to possess satisfactory storage stability at −5–0 °C.

We found that the yield of **1** depends, to a great extent, on the molar ratio of MeOK to bis-perchlorate **3** (2:1 30%; 4:1 60%; 6:1 94%).

Condensation of bis-aminaleacetal **1** with malonates **4a,b**, without catalysts, at room temperature affords novel trienic tetraesters **5a,b** (Scheme 2).[‡]

These reactions have shown, in principle, the possibility of involving both aminaleacetal groups in the condensation of bis-aminaleacetal **1**.

The results of studies on the condensation of bis-aminaleacetal **1** with various ketones and CH-acids will be the subject of our future publications.

[‡] *General procedure*. To a solution of **1** (0.5 g, 1.9 mmol) in dry benzene (2 ml) at room temperature was added malonate **4a** (0.43 ml, 3.8 mmol). The reaction mixture was allowed to stand for 24 h at room temperature, then the solvent was removed under reduced pressure, absolute ether was added to the oil residue and the mixture cooled to −70 °C. The resulting yellow powder was filtered off, washed with absolute ether to give 0.37 g **5a** (30%), mp 109–113 °C (from MeOH).

Spectroscopic data. Compound **5a**: ^{1}H NMR ($CDCl_3$): 7.52 (2H, s, H-β), 6.99 (1H, s, H-δ), 3.77 (6H, s, COOMe), 3.74 (6H, s, COOMe), 3.16 (6H, s, NMe_2); UV λ_{max}/nm (EtOH): 372 (ε 32600).

Compound **5b**: yield 31%; mp 92–94 °C; ^{1}H NMR ($CDCl_3$) 7.50 (2H, s, H-β), 6.95 (1H, s, H-δ), 4.22 (4H, q, CH_2), 4.19 (4H, q, CH_2), 3.14 (6H, s, NMe_2), 1.27 (6H, t, Me), 1.26 (6H, t, Me); UV λ_{max}/nm (EtOH): 372 (ε 21800).

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