Cascade cycloaddition reactions involving dimethylhydrazones of α-substituted acroleins

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Unusual cascade cycloaddition reactions with dimethylhydrazones of α-trimethylsilyloxyalkylacroleins acting as azadienes were found. Depending on the nature of the dienophile, the reactions give either fused heterocyclic compounds (when two consecutive Diels—Alder reactions take place) or azabicyclic compounds, resulting from the [2+4]- and [2+3]-cycloaddition cascade.

Key words: dimethylhydrazones, azadienes, cascade reactions, cycloaddition, dienophiles.

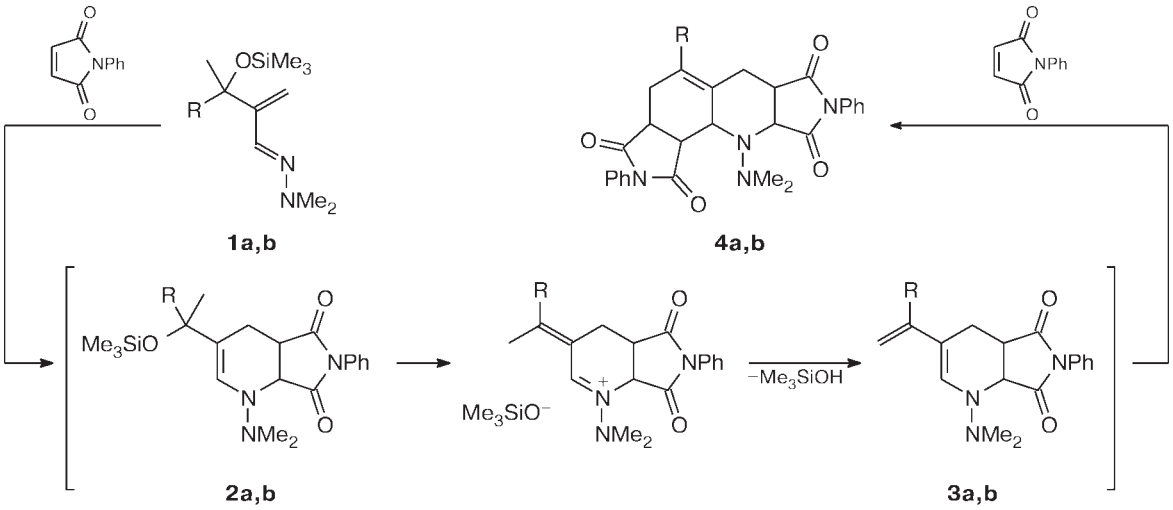
Hetero-Diels—Alder reaction is an efficient method for the formation of six-membered heterocycles.[1] In particular, 1-dimethylamino-1-azadienes or dimethylhydrazones of α,β-unsaturated carbonyl compounds are used in the synthesis of pyridine[2,3] and piperidine[3] derivatives. A specific feature of these dienes is higher reactivity in cycloaddition reactions compared to analogous oximes and imines because of mesomeric effect of the dimethylamino group.[4]

Previously,[5] we developed a general method for the synthesis of dimethylhydrazones of α-substituted acroleins including hydrazones **1**, containing the Me_3SiO group in the substituent.

This work is devoted to the study of reactions of these compounds with various dienophiles.

It was found that hydrazones **1a,b** react with *N*-phenylmaleimide even at ~20 °C and that the process does not stop at the stage of formation of cycloadducts **2a,b** (Scheme 1). In our opinion, this is due to the enhanced mobility of the Me_3SiO group in compound **2** caused by the mesomeric influence of the ring N atom. Dienes **3a,b** formed upon elimination of Me_3SiOH react with a sec-

Scheme 1



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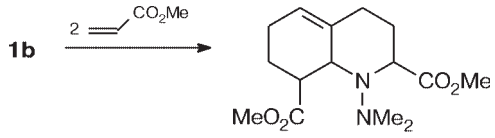
ond dienophile molecule to give final products **4a,b** in almost quantitative yields. Intermediates **2** and **3** were not isolated. This suggests that the primary cycloaddition is a slower process than the two subsequent transformations.

The reaction with methyl acrylate as a dienophile proceeds in a similar way (Scheme 2). The highest yield of product **5** is achieved when hydrazone **1b** is refluxed with a 10-fold excess of methyl acrylate for 24 h.

Scheme 2



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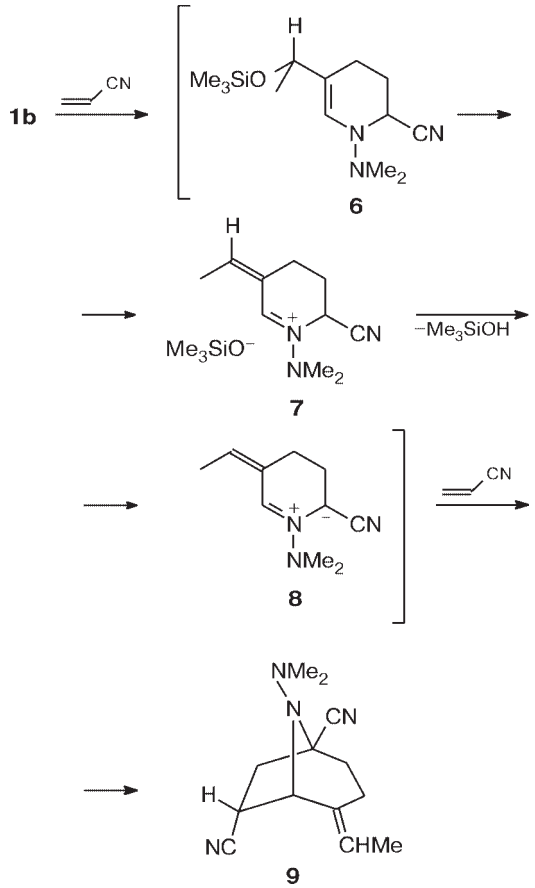
However, a different sequence of transformations is observed in the reaction of compound **1b** with acrylonitrile (Scheme 3). In our opinion, cycloadduct **6** formed in the first step undergoes thermal dissociation to give

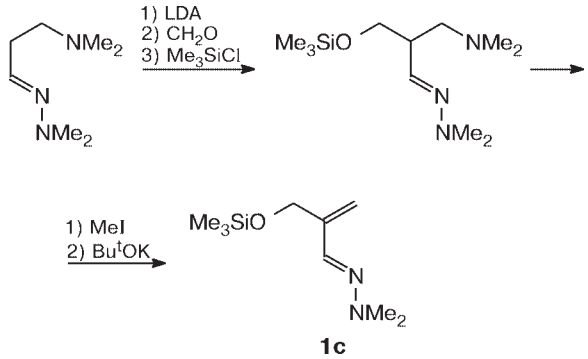
Scheme 3



immonium cation **7** and the Me_3SiO^- anion. The subsequent proton transfer between these species results in 1,3-dipole **8**, which undergoes [2+3]-cycloaddition with a second acrylonitrile molecule to give adduct **9**. This qualitative difference between the reactivity of acrylonitrile and those of methyl acrylate or *N*-phenylmaleimide is, apparently, due to the higher C—H acidity of the immonium cation **7** containing the C≡N group relative to cations in which the acidifying effect of the amide or ester group is weaker.

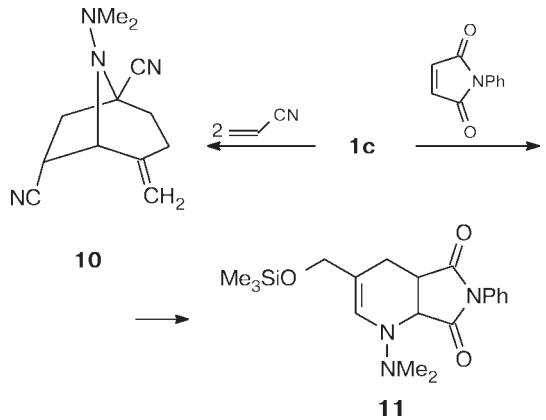
In order to carry out the [2+4]- and [2+3]-cycloaddition cascade with methyl acrylate, acrylonitrile, and *N*-phenylmaleimide as dienophiles, we prepared hydrazone **1c** (Scheme 4) whose adducts with dienophiles are unable to undergo elimination of Me_3SiOH to give a C=C bond.

Scheme 4



Indeed, acrylonitrile reacts with azadiene **1c** in the same way as with hydrazone **1b**, *i.e.*, to give bicyclic adduct **10** (Scheme 5).

Scheme 5



It was assumed that the same sequence of reactions would also take place with *N*-phenylmaleimide and me-

thyl acrylate as dienophiles. However, the reaction of hydrazone **1c** with *N*-phenylmaleimide stops after the formation of monoadduct **11**, which gradually polymerizes on storage.

The reaction of hydrazone **1c** with methyl acrylate proceeds under more drastic conditions to give a mixture of polymeric products. The attempts to carry out cycloaddition in the presence of an external base to generate a dipole were also unsuccessful.

Thus, we found two unusual cascade cycloaddition reactions having no analogs in the azadiene chemistry. It should be emphasized that both types of reaction are highly regio- and stereoselective and, in all cases, only one diastereomeric pair is formed.

Compounds **4b** and **10** were studied by X-ray diffraction analysis in order to determine their stereochemistry. The general view of molecules is shown in Figs. 1 and 2. Analysis of bond lengths and angles in cycloadducts **4b** and **10** (Table 1) showed that they are close to values typical of the given class of compound.

In compound **4b**, five-membered rings occupy *trans*-positions relative to the six-membered rings; the

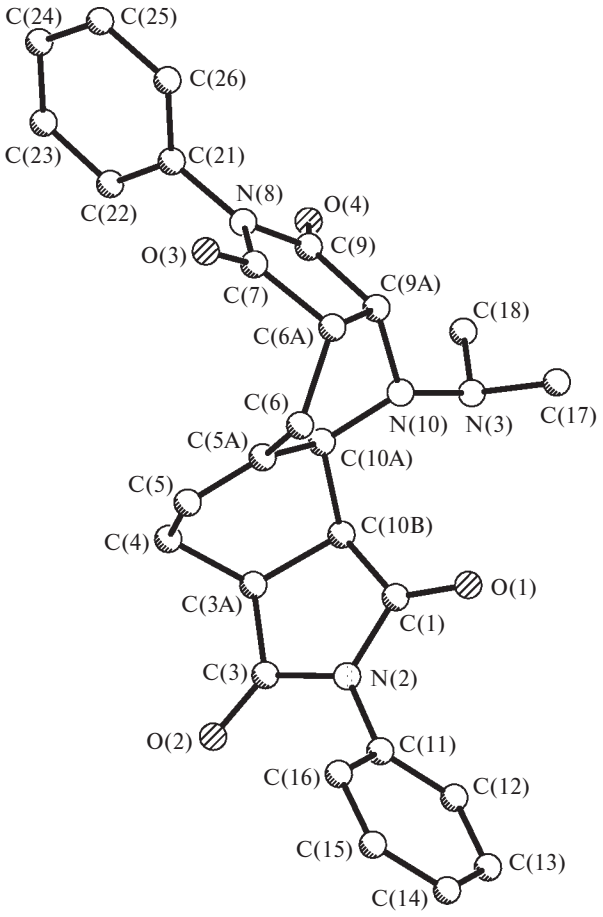


Fig. 1. General view of molecule **4b**.

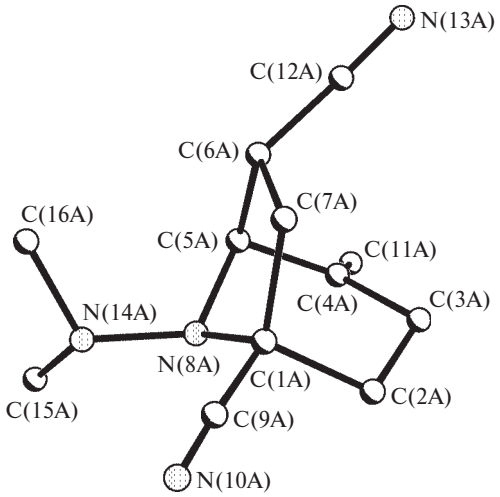


Fig. 2. General view of molecule **10**.

C(3)—C(3A)—C(4)—C(5), C(5)—C(5A)—C(6)—C(6A), C(1)—C(10B)—C(10A)—N(10), and N(10)—C(9A)—C(9)—N(8) torsion angles are 75.9(2), 134.8(2), 57.1(2), and 131.4(2)°, respectively.

The C(1)N(2)C(3)C(3A)C(10B) five-membered ring exists in a highly flattened envelope conformation; the C(10B) atom deviates from the envelope base by 0.06 Å, while the C(6A)C(7)N(8)C(9)C(9A) ring is in the half-chair conformation in which the C(6A) and C(9A) atoms deflect from the plane of other atoms by 0.11 and 0.06 Å, respectively. The N atoms in both rings (N(2) and N(8)) have planar conformations characterized by a sum of bond angles of 360°.

The phenyl substituents at the N(2) and N(8) endocyclic atoms are rotated with respect to the five-membered rings, the angles between the rings are, on average, 66.5°.

The C(10B)C(3A)C(4)C(5)C(5A)C(10A) six-membered ring has a boat conformation in which the C(4) and

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **4b**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(1)	1.204(2)	N(8)—C(21)	1.433(3)
O(2)—C(3)	1.201(2)	N(10)—C(10A)	1.445(2)
O(3)—C(7)	1.209(2)	N(10)—C(9A)	1.469(2)
O(4)—C(9)	1.198(2)	C(5)—C(5A)	1.316(3)
N(2)—C(3)	1.382(2)		
N(2)—C(1)	1.387(2)	Angle	ω/deg
N(2)—C(11)	1.431(2)		
N(3)—N(10)	1.425(2)	C(3)—N(2)—C(1)	113.19(16)
N(3)—C(18)	1.449(3)	C(7)—N(8)—C(9)	113.04(18)
N(3)—C(17)	1.456(3)	N(3)—N(10)—C(9A)	119.55(14)
N(8)—C(7)	1.387(3)	C(10A)—N(10)—C(9A)	111.49(15)
N(8)—C(9)	1.395(3)	C(5)—C(5A)—C(6)	126.44(17)

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compound **10**

Bond	*d*/Å
C(4)—C(11)	1.303
C(5)—N(8)	1.460
C(6)—C(7)	1.532
C(6)—C(12)	1.459
N(8)—N(14)	1.433
N(14)—C(15)	1.452
N(14)—C(16)	1.448

Angle	ω/deg
C(2)—C(1)—C(7)	110.5
C(3)—C(2)—C(1)	110.8
C(4)—C(3)—C(2)	113.0
C(3)—C(4)—C(5)	113.9
C(4)—C(5)—C(6)	112.0
C(7)—C(6)—C(5)	104.7
C(6)—C(7)—C(1)	102.5
C(12)—C(6)—C(5)	113.6
N(14)—N(8)—C(5)	119.7
N(14)—N(8)—C(1)	114.3
C(11)—C(4)—C(3)	123.5
C(11)—C(4)—C(5)	122.5

C(10A) atoms deviate from the plane formed by the other atoms by 0.54 and 0.66 Å, respectively, while the C(10A)C(5A)C(6)C(6A)C(9A)N(10) six-membered ring, fused with the last-mentioned ring along the C(5A)—C(10A) bond, has a distorted boat conformation with deviation of the C(6) and N(10) atoms by 0.54 and 0.68 Å, respectively. The N(10) nitrogen atom is pyramidal (the sum of bond angles is 345.0°).

In compound **10**, the unit cell contains four independent molecules (**A**, **B**, **C**, and **D**) in which the 8-azabicyclo[3.2.1]octane fragment has a boat—envelope conformation with the N(8) atom deviating from the envelope base by 0.59 Å. The key geometrical parameters of all molecules are close to each other; the differences are mainly related to the magnitude of deviation of the methylene group from the plane of the boat, which makes, on average, 0.31 Å in one pair of independent molecules (**A** and **D**) and 0.40 Å in the other pair (**B** and **C**). The endocyclic N(8) atom is pyramidal (the average sum of bond angles is 337.4°).

The cyano groups at C(1) and C(6) occupy intermediate positions relative to the root-mean-square plane of the boat and have *trans*-arrangement with respect to each other (the N(10)—C(9)—C(12)—N(13) pseudo-torsion angle is, on average, 87.4°).

Experimental

NMR spectra were recorded on a Bruker WM-400 (400 MHz) in $CDCl_3$. Elemental and X-ray diffraction analyses were carried out at the microanalytical and X-ray diffraction laboratories of the Institute of Organoelement Compounds of the RAS.

3-Dimethylamino-2-trimethylsilyloxymethylpropanal dimethylhydrazone. A 1.6 *M* solution of Bu^nLi (65.0 mL, 104 mmol) in hexane was added with stirring under argon to a solution of diisopropylamine (10.8 g, 15.0 mL, 107 mmol) in 170 mL of anhydrous THF cooled to −5 °C. After 5 min, β-dimethylaminopropionaldehyde dimethylhydrazone[6] (16.7 mL, 14.3 g, 100 mmol) was added to the solution at the same temperature, and the mixture was stirred for 1 h at 0 °C. Then the reaction mixture was cooled to −30 °C and paraformaldehyde (3.05 g, 102 mmol) was added. The mixture was stirred for 2 h at 0 °C and cooled to −40 °C, and Me_3SiCl (13.5 mL, 11.6 g, 106 mmol) was added dropwise over a period of 10 min. The mixture was allowed to stand for 1 h at 0 °C and treated with 20 mL of a 5% aqueous solution of K_2CO_3. The organic layer was separated and the aqueous layer was extracted with ether (3×40 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*, and the residue was distilled. Yield 17.9 g (73%), b.p. 75 °C (1 Torr). Found (%): C, 53.78; H, 11.01; N, 17.20. $C_{11}H_{27}N_3OSi$. Calculated (%): C, 53.83; H, 11.09; N, 17.12. ^{1}H NMR, δ: 0.07 (s, 9 H, Me_3Si); 2.20 (s, 6 H, $\underline{Me}_2NCH_2$); 2.35—2.60 (m, 3 H, $CH_2C\underline{H}$); 2.73 (s, 6 H, Me_2NN); 3.68 (d, 2 H, CH_2O, J = 5.6 Hz); 6.55 (d, 1 H, CH=N, J = 7.0 Hz).

2-Trimethylsilyloxymethylacrolein dimethylhydrazone (1c). A solution of MeI (10.5 g, 4.6 mL, 74 mmol) in 20 mL of THF was added dropwise under argon with stirring and cooling to 0 °C over a period of 10 min to a solution of 3-dimethylamino-2-trimethylsilyloxymethylpropanal dimethylhydrazone (17.9 g, 73 mmol) in 150 mL of THF. The reaction mixture was allowed to stand for 12 h and cooled to −30 °C and Bu^tOK (8.20 g, 73.5 mmol) was added. The mixture was stirred for 3 h at 20 °C and treated with 50 mL of a 20% aqueous solution of NaCl. The organic layer was separated and the aqueous layer was extracted with ether (3×40 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*, and the residue was distilled to give 7.86 g of a mixture containing, in addition to the target product, 37 mol.% of 2-hydroxymethylacrolein dimethylhydrazone (according to ^{1}H NMR spectroscopy). The mixture was dissolved in 70 mL of THF; Me_3SiCl (1.22 mL, 1.03 g, 9.4 mmol) and Et_3N (1.5 mL, 1.09 g, 10.8 mmol) were added and the mixture was refluxed for 2 h. After cooling, 30 mL of hexane was added and the $Et_3N \cdot HCl$ precipitate was filtered off and washed with 20 mL of hexane. The filtrate was concentrated *in vacuo* and the residue was distilled to give 7.09 g (48%) of hydrazone **1c,** b.p. 53—54 °C (1 Torr). Found (%): C, 53.88; H, 10.01; N, 14.05. $C_9H_{20}N_2OSi$. Calculated (%): C, 53.95; H, 10.06; N, 13.98. ^{1}H NMR, δ: 0.13 (s, 9 H, Me_3Si); 2.82 (s, 6 H, Me_2N); 4.42 (s, 2 H, CH_2O); 5.15, 5.42 (both d, each 1 H, CH_2=, J = 1.6 Hz); 7.03 (s, 1 H, CH=). ^{13}C NMR, δ: −0.52 (Me_3Si); 42.4 (Me_2N); 61.0 (CH_2O); 113.0 ($\underline{C}H_2$=C); 134.2 (CH=N); 144.9 (CH_2=$\underline{C}$).

10-Dimethylamino-5-methyl-2,8-diphenyl-1,2,3a,4,6,6a,7,8,9a,10,10a,10b-dodecahydrodipyrrolo[3,4-*b*;3,4-*h*]quinoline-1,3,7,9-tetrone (4a). A mixture of hydrazone **1a** (0.57 g, 2.5 mmol) and *N*-phenylmaleimide (0.865 g, 5.0 mmol) in 4 mL of CH_2Cl_2 was allowed to stand for 24 h at 20 °C. The solvent was distilled *in vacuo* and the solid residue was recrystallized from dioxane to give 1.056 g (80%) of compound **4a**, m.p. 210—211 °C (with dec.). Found (%): C, 67.95; H, 6.11; N, 10.51. $C_{28}H_{28}N_4O_4 \cdot 0.5C_4H_8O_2$. Calculated (%): C, 68.10; H, 6.11; N, 10.60. ^{1}H NMR, δ: 1.70 (s, 3 H, Me); 2.40—2.60, 2.65—2.75, 2.85 (all m, 10 H, $H_2C(4)$, $H_2C(6)$, NMe_2); 3.25, 3.40 (both t, each 1 H, H(3a), H(6a), J = 7.3 Hz); 3.70 (m, 1 H, H(10a)); 4.00 (dd, 1 H, H(10b), J = 8.2 Hz, J = 5.4 Hz); 4.72 (d, 1 H, H(2), J = 8.9 Hz); 7.05—7.13, 7.38—7.50 (both m, 10 H, Ar). ^{13}C NMR, δ: 18.8 (Me); 25.0, 31.6 (C(4), C(6)); 39.5, 41.3,

41.9, 43—44, 53.2, 57.7 (C(3a), C(6a), C(9a), C(10a), C(10b), NMe_2); 126—132 (Ar, C(5), C(5a)); 174.8, 175.7, 177.4, 178.4 (C(1), C(3), C(7), C(9)).

10-Dimethylamino-2,8-diphenyl-1,2,3a,4,6,6a,7,8,9a,10,10a,10b-dodecahydrodipyrrolo[3,4-*b*;3,4-*h*]quinoline-1,3,7,9-tetrone (4b). A mixture of hydrazone **1b** (0.535 g, 2.5 mmol) and *N*-phenylmaleimide (0.865 g, 5.0 mmol) in 4 mL of CH_2Cl_2 was allowed to stand for 24 h at 20 °C. White crystals precipitated from the solution; they were filtered off, washed with cold CH_2Cl_2, and dried *in vacuo* to give 1.11 g (80%) of compound **4b**, m.p. 241—242 °C (with dec.). Found (%): C, 60.60; H, 5.15; N, 10.01. $C_{27}H_{26}N_4O_4 \cdot CH_2Cl_2$. Calculated (%): C, 60.53; H, 5.08; N, 10.09. ^{1}H NMR, δ: 2.27—2.35 (m, 1 H, H(4)); 2.57—2.61, 2.70, 2.75—2.9 (all m, 9 H, $H_2C(4)$, $H_2C(6)$, NMe_2); 3.25 (t, 1 H, H(3a), J = 7.6 Hz); 3.37 (td, 1 H, H(6a), J = 8.3 Hz, J = 2.5 Hz); 3.77 (m, 1 H, H(10a)); 4.02 (dd, 1 H, H(10b), J = 8.6 Hz, J = 5.4 Hz); 4.66 (d, 1 H, H(9a), J = 8.9 Hz); 5.79 (m, 1 H, HC(5)); 7.10—7.20, 7.35—7.50 (both m, 10 H, Ar).

1-Dimethylamino-6-phenyl-3-trimethylsilyloxymethyl-1,4,4a,5,6,7a-hexahydropyrrolo[3,4-*b*]pyridine-5,7-dione (11). A mixture of hydrazone **1c** (0.57 g, 2.5 mmol) and *N*-phenylmaleimide (0.432 g, 2.5 mmol) in 4 mL of CH_2Cl_2 was allowed to stand for 24 h at ~20 °C. The solvent was evaporated *in vacuo*, the residue was dissolved in 15 mL of CCl_4, hexane (15 mL) was added, the solution was filtered, and the solvents were evaporated *in vacuo*. The yield of compound **11** was 0.746 g (80%), oil. Found (%): C, 60.95; H, 7.20; N, 11.34. $C_{19}H_{27}N_3O_3Si$. Calculated (%): C, 61.10; H, 7.29; N, 11.25. ^{1}H NMR, δ: 0.14 (s, 9 H, Me_3Si); 2.03—2.12 (m, 1 H, $H(CH_2)$); 2.61 (s, 6 H, NMe_2); 2.62—2.75 (m, 1 H, $H(CH_2)$); 3.00 (dd, 1 H, NCHC<u>H</u>, J = 8.1 Hz, J = 16.2 Hz); 4.05 (s, 2 H, OCH_2); 4.31 (d, 1 H, NCH, J = 8.1 Hz); 6.34 (s, 1 H, CH=); 7.26—7.50 (m, 6 H, Ar). ^{13}C NMR, δ: −0.5 ($SiMe_3$); 23.1 (C(4)); 36.9 C(4a)); 43.1 (NMe_2); 56.5 (C(7a)); 64.7 (CH_2OSi); 106.4 (C(3)); 126.0 (C_m); 127.0 (C(2)); 128.2 (C_p); 128.8 (C_o); 131.5 (C_{ipso}); 175.1, 176.2 (2 CO).

8-Dimethylamino-4-ethylidene-8-azabicyclo[3.2.1]octane-1,6-dicarbonitrile (9). A mixture of hydrazone **1b** (0.92 g, 4.3 mmol) and 2.2 mL of freshly distilled acrylonitrile was refluxed for 11 h. After cooling, white crystals precipitated from the solution; they were filtered off, washed with a small amount of cold ether, and dried *in vacuo* to give 0.79 g (80%) of compound **9**, m.p. 86—88 °C. Found (%): C, 67.70; H, 7.95; N, 24.20. $C_{13}H_{18}N_4$. Calculated (%): C, 67.80; H, 7.88; N, 24.33. ^{1}H NMR, δ: 1.67 (m, 3 H, Me); 1.80—1.86, 2.25—2.36, 2.38—2.48 (all m, 4 H, 2 CH_2); 2.55 (s, 6 H, NMe_2); 2.69—2.83 (m, 2 H, CH_2); 3.26—3.33 (m, 1 H, CHCN); 4.11 (d, 1 H, CHN, J = 6.4 Hz); 5.43—5.50 (m, 1 H, CH_3C<u>H</u>). ^{13}C NMR, δ: 12.5 (CH_3); 19.3 (CH_2); 30.5 (CH_2); 30.6 (<u>C</u>HCN); 37.0 (CH_2); 46.8 (NMe_2); 60.2 (NC); 63.0 (N—CH); 118.4, 120.1 (2 CN); 124.0 (CH=); 130.9 (CH=<u>C</u>).

8-Dimethylamino-4-methylidene-8-azabicyclo[3.2.1]octane-1,6-dicarbonitrile (10). A mixture of hydrazone **1c** (0.68 g, 3.4 mmol) and 4.0 mL of freshly distilled acrylonitrile was refluxed for 11 h. The solvent was evaporated *in vacuo*. The residue was dissolved in 15 mL of CCl_4, hexane was added until crystallization started, and the mixture was allowed to stand for ~12 h. The resulting crystals were filtered off, quickly washed with a small amount of cold CCl_4, and dried *in vacuo* to give 0.42 g (60%) of compound **10**, m.p. 100.5—101.5 °C. Found (%): C, 66.50; H, 7.40; N, 25.95. $C_{12}H_{16}N_4$. Calculated (%): C, 66.64; H, 7.46; N, 25.90. ^{1}H NMR, δ: 1.80—1.87, 2.29—2.36, 2.45—2.65 (all m, 6 H, 3 CH_2); 2.55 (s, 6 H, NMe_2); 3.32—3.39 (dt, 1 H, CHCN, J = 12.2 Hz, J = 6.2 Hz); 4.23 (d, 1 H, CHN, J = 6.2 Hz); 5.01, 5.06 (both s, each 1 H, CH_2=C). ^{13}C NMR, δ: 24.7 (C(2)); 30.2 (C(6)); 31.2 (C(7)); 37.0 (C(3)); 46.7 (NMe_2); 60.1 (C(1)); 62.0 (C(5)); 114.6 (<u>C</u>H_2=C); 118.4, 119.9 (2 CN); 139.7 (C(4)).

Dimethyl-1-dimethylamino-1,2,3,4,6,7,8,8a-octahydroquinoline-2,8-dicarboxylate (5). A mixture of hydrazone **1b** (3.77 g, 17.6 mmol) and 12 mL of freshly distilled methyl acrylate was refluxed for 15 h. The solution was concentrated *in vacuo* and the residue was distilled to give 3.87 g (75%) of compound **5**, b.p. 130—140 °C (1 Torr). Found (%): C, 60.68; H, 8.10; N, 9.53. $C_{15}H_{24}N_2O_4$. Calculated (%): C, 60.79; H, 8.16; N, 9.45. ^{1}H NMR, δ: 1.80—2.10 (m, 8 H, CH_2); 2.23 (s, 6 H, Me_2N); 2.92 (m, 1 H, H(8)); 3.59, 3.64 (both s, each 3 H, 2 MeO); 3.87—3.90 (m, 1 H, H(8a)); 4.55 (m, 1 H, H(2)); 5.38 (s, 1 H, H(5)). ^{13}C NMR, δ: 22.2, 23.5 (C(3), C(7)); 29.1, 29.6 (C(4), C(6)); 42.0—43.0 (Me_2N); 42.3 (C(8)); 50.6, 51.4 (C(2), C(8a)); 51.9, 56.0 (CH_3O); 120.7 (C(5)); 135.0 (C(4a)); 173.3, 176.4 (CO_2Me).

X-ray diffraction study of compounds 4b and 10. The crystals of compounds **4b** and **10** were prepared by crystallization from CH_2Cl_2 and from a 2 : 1 hexane—dioxane mixture, respectively.

Table 3. X-Ray experiment and structure refinement details for compounds **4b** and **10**

Parameter	Structure	
	4b	**10**
Diffractometer	CAD 4	SMART 1000K CCD
Molecular formula	$C_{28}H_{28}Cl_2N_4O_4$	$C_{12}H_{16}N_4$
Molecular weight	555.4	216.29
Crystal size/mm	0.5×0.3×0.1	0.4×0.4×0.2
T/K	298	110
Radiation	λ-Mo-Kα (0.71072 Å)	
Space group	$P1$	$Pna2_1$
a/Å	9.531(2)	27.77(2)
b/Å	12.368(3)	7.197(6)
c/Å	12.967(3)	23.29(2)
α/deg	69.15(3)	
β/deg	73.45(3)	
γ/deg	76.86(3)	
V/Å^3	1355.8(5)	
Z	2	16
d_{calc}/g cm^{-3}	1.361	1.234
μ/cm^{-1}	2.81	0.78
F(000)	580	1856
Scan mode	θ/(5/3θ)	ω
$2\theta_{max}$/deg	25.00	27.00
The number of independent reflections	4757	8591
R_1 (over F for reflections with $I > 2\sigma(I)$)	0.0453(2921)	0.082(6092)
wR_2 (over F^2 for all reflections)	0.1398	0.1934
The number of refined parameters	441	833

The main crystallographic data, X-ray experiment details, and structure refinement data are listed in Tables 1 and 2. The structures were solved by the direct method and refined by the least-squares method in the anisotropic approximation over F^2 in the full-matrix isotropic-anisotropic approximation. In the case of compound **4b**, analysis of the difference Fourier syntheses around the CH_2Cl_2 solvation molecule showed that the Cl atoms are disordered in 1 : 1/3 ratio. The H atoms were located from electron density difference Fourier syntheses and refined isotropically, except for the H atoms in the CH_2Cl_2 molecule, which were calculated geometrically and refined according to the "riding" model. Full tables of atom coordinates, thermal factors, bond lengths, and bond angles are deposited with the Cambridge Structural Database (CSDB).

The calculations were carried out on IBM PC using a SHELX-97 program package.

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References

1. D. L. Boger, *Chem. Rev.*, 1986, **86**, 781; D. L. Boger and S. W. Weinreb, *Hetero Diels—Alder Methodology in Organic Synthesis*, Academic Press, New York, 1987.
2. E. Pascual-Alfonso, C. Avendano, and J. C. Menendez, *Synlett*, 2000, 205.
3. J. Barluenga and M. Tomas, *Adv. Heterocycl. Chem.*, 1993, **189**, 1.
4. H. Waldman, *Synthesis*, 1994, 535.
5. N. P. Tsvetkov, V. E. Vakhmistrov, A. B. Koldobsky, and V. N. Kalinin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1707 [*Russ. Chem. Bull.*, 1999, **48**, 1685 (Engl. Transl.)].
6. A. B. Koldobsky, V. E. Vakhmistrov, and V. N. Kalinin, *Dokl. Akad. Nauk*, 1996, **346**, 771 [*Dokl. Chem.*, 1996 (Engl. Transl.)].

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