Aminals in the synthesis of 1,3-substituted propargylamines and 3*H*-2-vinylidene-3-aminobenzofuran derivatives

L. Yu. Ukhin,[a] V. N. Komissarov,[a] S. V. Lindeman,[b] V. N. Khrustalev,[b] and Yu. T. Struchkov[b]*

[a]*Institute of Physical and Organic Chemistry, Rostov State University, 194/3 prosp. Stachki, 344771 Rostov-on-Don, Russian Federation. Fax: +7 (863) 228 5667*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

Aminals of aromatic *o*-hydroxyaldehydes react when heated with terminal acetylenes to form, depending on the reaction conditions and the nature of the starting compounds, 1,3-substituted propargylamines or 3*H*-2-vinylidene-3-aminobenzofuran derivatives, the structures of which were established by X-ray diffraction.

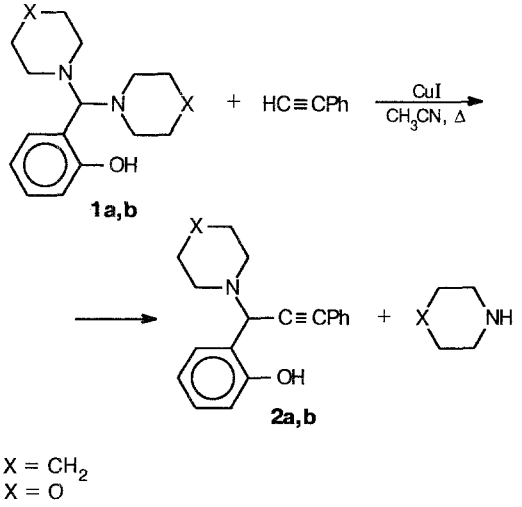
Key words: aminals of *o*-hydroxyaldehydes; substituted propargylamines; 3*H*-2-vinylidene-3-aminobenzofuran derivatives; X-ray diffraction.

Previously[1] we have demonstrated that aminals of aromatic aldehydes react with terminal acetylenes in the presence of CuI to form 1,3-substituted propargylamines.

In this work, we studied the reaction of terminal acetylenes with aminals of aromatic *o*-hydroxyaldehydes; we demonstrated that these reactions, depending on the reaction conditions and the nature of the starting compounds, may result in 1,3-substituted propargylamines or the products of their cyclization, 3*H*-2-vinylidene-3-aminobenzofuran derivatives.

Salicylaldehyde aminals (**1a,b**) react with phenylacetylene in boiling acetonitrile in the presence of CuI to give propargylamines (**2a,b**) (Scheme 1).

Scheme 1



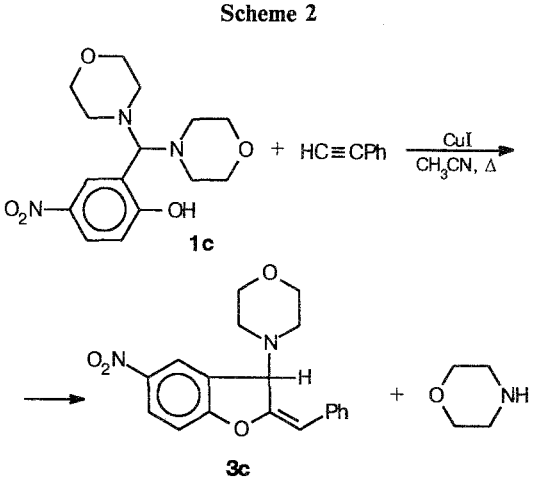
Under the same conditions, morpholinal of 5-nitrosalicylaldehyde **1c** gives 3*H*-2-benzylidene-3-morpholino-5-nitrobenzofuran (**3c**) (Scheme 2).

Aminals of salicylic and 5-nitrosalicylic aldehydes react with propargyl alcohol, its phenyl ether, and dimethylethynylcarbinol to form benzofuran derivatives (**3a,b,d,e**) (Scheme 3).

When heated without the solvent and CuI, aminals **1a—c** react with phenylacetylene to form only propargylamines of structure **2**, and the reaction proceeds considerably faster (2—5 min) than the reaction with 2,6-di-*tert*-butylphenol (0.5—1 h).[2]

In another experiment, we demonstrated that boiling 1-phenyl-3-(2-hydroxy-5-nitrophenyl)-3-morpholinopropyne (**2c**) with CH_3CN in the presence of CuI results

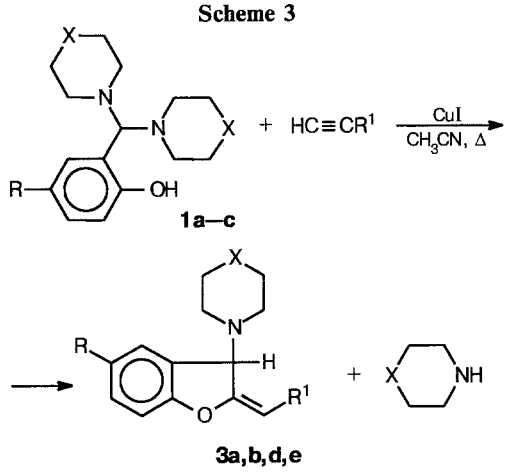
Scheme 2



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 455—460, March, 1994.

1066-5285/94/4303-0413 $12.50

Scheme 3



3a: R = NO_2, R^1 = CH_2OH, X = O
3b: R = H, R^1 = CH_2OPh, X = O
3d: R = NO_2, R^1 = $C(CH_3)_2OH$, X = O
3e: R = H, R^1 = $C(CH_3)_2OH$, X = CH_2

in gradual cyclization of **2c** to benzofuran **3c.** When small amounts of morpholine are added, this conversion becomes fast and quantitative. It is therefore concluded that the soluble morpholine complex with CuI is the active agent, inducing cyclization, whereas the presence of copper iodide or its complex is a necessary, but sometimes not sufficient condition for the cyclization of propargylamines. The acidity of phenolic hydroxyl is of considerable importance: when propargyl alcohol, its ether, or dimethylethynylcarbinol are used, the acidity of the salicylic derivative is sufficient, whereas in the case of phenylacetylene, cyclic products are formed only with aminals of 5-nitrosalicylaldehyde. The aminomethylation of acetylene is apparently possible only at a certain level of its acidity. This is evident from the inertness of *p*-methoxyphenylacetylene to aminals: *p*-methoxyphenylacetylene, which is isolated from reactions performed both in the presence and in the absence of copper iodide, remains intact.

A characteristic feature of the prepared propargylamines is the absence of stretching bands of the triple C≡C bond and of the hydroxyl group in the IR spectra, and of the signal of the hydroxyl group in the ^1H NMR spectrum. The latter is so much broadened that, under normal conditions, it is observed only when integrated in the 10—13 ppm region.

The structure of the propargylamines was established by X-ray diffraction of compound **2b**. The overall view of the molecule is shown in Fig. 1. Bond lengths and bond angles for molecule **2b** are close to the normal values.[3] The four-atom fragment with the triple C(8)≡C(9) bond is virtually linear (the angles C(7)C(8)C(9) and C(8)C(9)C(11) are 179.7(3) and 177.5(3)°, respectively). The morpholine cycle has a nearly ideal chair conformation (the endocyclic angles are 56.8(3)—59.3(3)°). The bulky 1-(2-hydroxyphenyl)3-phenylpropyl substituent is in an equatorial position with respect to the morpholine heterocycle; its orientation, which is characterized by the C(2)—C(7)—N(21)—C(22) torsion angle of 68.5°, is determined by the closure of the intramolecular hydrogen bond O(1)—H···N(21) (O···N is 2.720(4), N···H is 1.75(4) Å, the O—H···N angle is 153(3)°). The presence of the hydrogen bond is evidently responsible for anomalies of the spectra of **2b** and its analogs.

The benzofuran derivatives **3** are stable in acidic media and are inert relative to strong acylating agents. They react with acetyl perchlorate ($HClO_4$ solution in acetic anhydride) and with perchloric acid to form stable and readily crystallizing perchlorates. Their structures

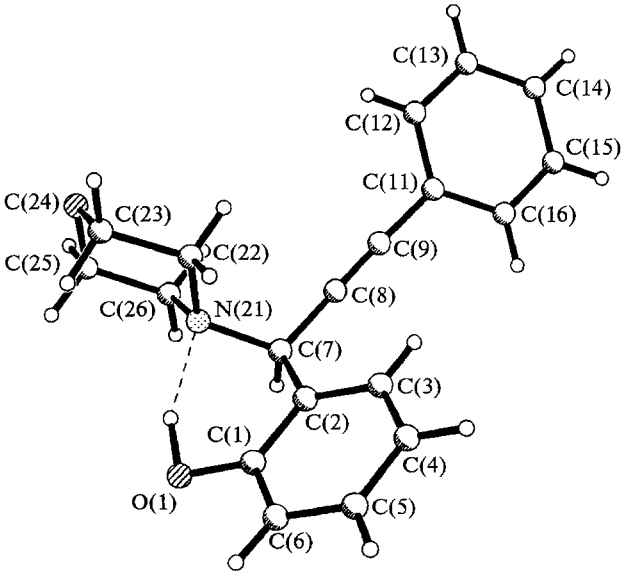


Fig. 1. The overall view of molecule **2b**.

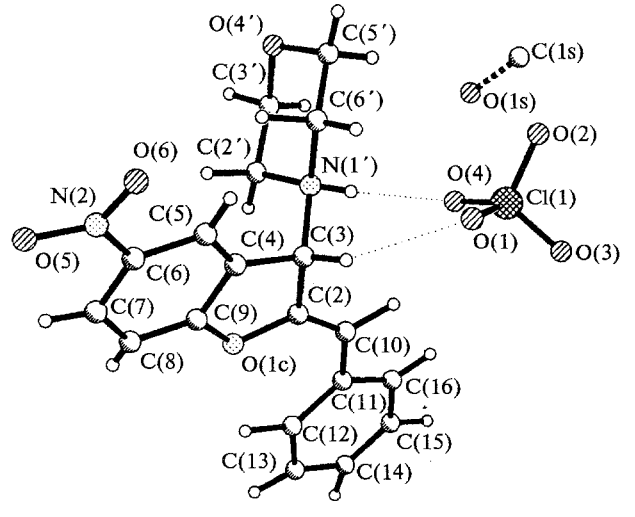


Fig. 2. The asymmetric part of the crystal structure **3c** · $HClO_4$.

were established by X-ray diffraction of one of these salts, namely, 3*H*-2-benzylidene-3-morpholino-5-nitrobenzofuran perchlorate (**3c**). The asymmetrical part of the crystal structure is shown in Fig. 2. The bond lengths and bond angles of the molecule of perchlorate **3c** have normal values[3] within relatively poor accuracy (due to the poor quality of the crystals). The benzovinylidenefuran fragment of the cation is essentially planar (none of the atoms deviates by more than 0.03(2) Å from its mean plane). There is no twisting about the double bond (the C(3)—C(2)=C(10)—C(11) torsion angle is 180.0(8)°).

The morpholine substituent has a nearly ideal chair conformation (the endocyclic torsion angles are 53.0(9)—63.3(9)°). The mutual orientation of the morpholine substituent (the N(1')—C(3) bond is equatorial) and the major portion of the molecule is characterized by the torsion angles C(2)—C(3)—N(1')—C(6') and C(4)—C(3)—N(1')—C(2') of 179.7(8) and 60.4(8)°, respectively. The orientation of the nitro group with respect to the central bicyclic nucleus and the orientation of the phenyl substituent with respect to the plane of the C(2)=C(10) double bond are characterized by angles of 10.3(9) and 6.6(9)°, respectively. The hydrogen atom, which is involved in the N(1')—H···O(4) hydrogen bond with the ClO_4^- anion (N(1')···O(4) is 2.88(2), H···O(4) is 2.1(2) Å, the N(1')—H···O(4) angle is 176(4)°), is in an axial position at the N(1') ammonium nitrogen atom. Evidently, the C(3)—H group also forms a weak hydrogen bond with ClO_4^- (C(3)···O(1) is 3.31(2), H···O(1) is 2.5(2), C(3)—H is 1.0(1) Å, the C(3)—H···O(1) angle is 145(4)°). In the crystal, the solvate methanol molecule has no contacts that could be interpreted in terms of hydrogen bonds. Apparently, its disorder and partial occupancy result from this fact.

Indirect evidence for the presence of hydrogen bonds can be obtained from the IR spectrum of perchlorate **3c**: the lowering of the symmetry of the ClO_4^- anion gives rise to the splitting of its characteristic absorption band in the region of 1100 cm^{-1} into several components, as was described for covalently bonded perchlorates.[4]

In the IR spectra of vinylidenebenzofurans **3a—e**, bands with moderate intensity are always present in the region of 1700 cm^{-1}, these bands can be assigned to the stretching vibrations of the exocyclic double bond conjugated with the furan oxygen atom. It is known,[5,6] that the vinyl ether fragments in 4*H*-benzopyranes are characterized by unusually large values of the double-bond frequencies.

Experimental

IR spectra were recorded on a Specord IR-75 instrument in vaseline oil. The ^1H NMR spectra were recorded on a Varian XL-100 spectrometer (compounds **2d, 3d,e**) using HMDS as the internal standard and on a Varian XL-300 spectrometer (compounds **2a,c, 3a—c**).

Salicylaldehyde aminals **1a,b** were prepared according to procedures described previously.[2]

2-Hydroxy-5-nitrophenyl-di(morpholino)methane (5-nitrosalicylaldehyde morpholinal, 1c). 5-Nitrosalicylaldehyde (10 g) was dissolved with heating in isopropyl alcohol (30 mL). Morpholine (10 mL) was added to the hot solution, and the mixture was held for 1 h. After rubbing slightly with a stick, fast crystallization was initiated. Then heptane (10 mL) was added to the solidified substance, the product was filtered off, washed with a 1:1 2-propanol—heptane mixture, then with heptane, and dried. The yield of **1c** was 18.6 g (96 %). Nearly colorless crystals were obtained after recrystallization from toluene. The compound has no exact melting point: the compound begins to change above 122 °C and at 142—148 °C turns to an orange material. Found (%): C, 55.00; H, 6.20; N, 12.35. $C_{15}H_{21}N_3O_5$. Calculated (%): C, 55.73; H, 6.50; N, 13.00. IR, ν/cm^{-1}: 1614, 1581 (arom.), 1523, 1341 (NO_2).

3-(2-Hydroxyphenyl)-1-phenyl-3-piperidinoprop-1-yne (2a).

a. A solution of aminal **1a** (2.74 g, 10 mmol), CuI (1.9 g, 10 mmol), and phenylacetylene (1.3 mL, 10.5 mmol) in MeCN (20 mL) was boiled for 30 min, the mixture was cooled, and an oil with a yellow precipitate was obtained after treatment with water and concentrated NH_4OH. The product was extracted with hot 2-propanol, the solution was filtered off, and then treatment with water gave a colorless precipitate; the precipitate was recrystallized from MeOH. The yield of **2a** was 0.7 g (24 %), m.p. 72—75 °C. Found (%): C, 82.58; H, 7.10; N, 5.10. $C_{20}H_{21}NO$. Calculated (%): C, 82.47; H, 7.22; N, 4.81.

b. A solution of aminal **1a** (1 g) in phenylacetylene (1 mL) was boiled for 5 min, placed into a Petri dish, and evaporated with a syringe with heating and petroleum ether and then MeOH were added. After cooling and triturating, the product was recrystallized from MeOH, washed on a filter with cold MeOH, and dried. The yield of **2a** was 0.55 g (52 %), m.p. 72—75 °C. Found (%): C, 82,89; H, 7.47; N, 4.98. $C_{20}H_{21}NO$. Calculated (%): C, 82.47; H, 7.22; N, 4.81. IR, ν/cm^{-1}: 1607, 1587, 1581 (arom.), 1274, 1250 (ν(C—O), δ (O—H)), 754, 688 (the monosubstituted benzene ring). The ^1H NMR ($CDCl_3$, δ): 1.30—1.75 (m, 6 H, CH_2); 2.70 (m, 4 H, CH_2N); 5.10 (s, 1 H, CH); 6.80—7.60 (m, 9 H, arom.); 9.70—13.50 (s, 1 H, OH).

3-(2-Hydroxyphenyl)-3-morpholino-1-phenyl-prop-1-yne (2b).

a. A mixture of salicylaldehyde morpholinal **1b** (5.56 g, 20 mmol), phenylacetylene (2.24 g, 22 mmol), and CuI (3.81 g, 10 mmol) was boiled in anhydrous MeCN (15 mL) for 30 min. The solution was cooled, then concentrated NH_4OH (20 mL) and water (70 mL) were added; the solution was extracted with $CHCl_3$ (2×20 mL), the extract was dried over anhydrous Na_2SO_4, and filtered off, and evaporated. The oil obtained was triturated with hexane, and the solid substance obtained was recrystallized from 15 mL of MeOH. The yield of **2b** was 4.7 g (75.1 %), m.p. 100—101 °C. Found (%): C, 77.20; H, 6.61; N, 5.10. $C_{19}H_{19}NO_2$. Calculated (%): C, 77.82; H, 6.48; N, 4.78.

b. A solution of aminal **1b** (0.5 g, 1.8 mmoles) in phenylacetylene (1 mL) was boiled for 15 min, placed into a Petri dish, and evaporated with heating while isooctane was added. The solution was extracted several times with boiling isooctane, and the extract was held overnight. The crystals obtained were separated and recrystallized from MeOH. The yield of **2b** was 0.26 g (52 %), m.p. 100—101 °C. Found (%): C, 77.71; H, 6.64; N, 4.60. $C_{19}H_{19}NO_2$. Calculated (%): C, 77.82; H, 6.48; N, 4.78. IR, ν/cm^{-1}: 1607, 1580, 1567 (arom.), 1274, 1254, 1234 (ν(C—O), δ(O—H)), 1107 (C—O—C), 750, 687 (the monosubstituted benzene ring). The ^1H NMR ($CDCl_3$,

δ): 2.72 (t, 4 H, CH_2N); 3.75 (t, 4 H, CH_2O); 5.12 (s, 1 H, CH); 6.77—7.56 (m, 8 H, arom.).

3-(2-Hydroxy-5-nitrophenyl)-3-morpholino-1-phenyl-prop-1-yne (2c). A solution of aminal **1c** (0.5 g, 1.5 mmol) in phenylacetylene (1 mL) was boiled for 3 min, octane (10 mL) was added, and then the solution was cooled. The rose-colored precipitate was filtered off and recrystallized twice from octane. The yield of **2c** was 0.28 g (52 %), m.p. 158—165 °C. Found (%): C, 67.20; H, 5.54; N, 8.22. $C_{19}H_{18}N_2O_4$. Calculated (%): C, 67.45; H, 5.33; N, 8.28. IR, ν/cm^{-1}: 1621, 1587 (arom.), 1527, 1514, 1341 (NO_2), 1281 (ν(C—O), δ(OH)), 1114 (C—O—C), 754, 698 (the monosubstituted benzene ring). The ^{1}H NMR ($CDCl_3$, δ): 2.84 (m, 4 H, CH_2N); 3.82 (m, 4 H, CH_2O); 5.10 (s, 1 H, CH); 6.85 (d, 1 H, C(3)—H of the 2-hydroxy-5-nitrophenyl substituent); 7.37 (m, 3 H, protons of the phenyl ring); 7.47 (m, 2 H, protons of the phenyl ring); 8.15 (d, 1 H, C(4)—H of the 2-hydroxy-5-nitrophenyl substituent); 8.52 (d, 1 H, C(6)—H of the 2-hydroxy-5-nitrophenyl substituent).

2-Hydroxymethylvinylidene-3-morpholino-5-nitro-3*H*-benzofuran (3a). A mixture of aminal **1c** (1.6 g, 5 mmoles), MeCN (10 mL), propargyl alcohol (0.5 mL, 8 mmoles), and CuI (0.5 g, 5 mmoles) was boiled with stirring for 30 min, cooled, and then concentrated NH_4OH (20 mL) and water (60 mL) were added; the solution was extracted with several portions of $CHCl_3$, and then the solvent was evaporated. The oily precipitate was extracted repeatedly with the same portion of boiling octane, and the precipitate, obtained after cooling with ice water, was filtered off, dried on a filter, and recrystallized from heptane. The yield of **3a** was 1 g (70 %). A light-yellow crystalline precipitate was formed, which was caramelized at ~20 °C to an orange material. Prior to analysis, the substance was dried under a vacuum at 100 °C. Found (%): 57.41; H, 5.35; N, 9.46. $C_{14}H_{16}N_2O_5$. Calculated (%): C, 57.53; H, 5.48; N, 9.59. IR, ν/cm^{-1}: 3367 (OH), 1700 (C=C), 1621, 1601 (arom.), 1527, 1341 (NO_2). The ^{1}H NMR ($CDCl_3$, δ): 2.48 (m, 2 H, CH_2N); 2.65 (m, 2 H, CH_2N); 3.67 (m, 4 H, CH_2O); 4.45 (m, 2 H, CH_2OH); 4.88 (s, 1 H, CH); 5.30 (t, 1 H, =CH—); 6.98 (d, C(7)—H arom.); 8.22 (dd, 1 H, C(6)—H, arom.); 8.25 (d, 1 H, C(4)—H, arom.).

3-Morpholino-3*H*-2-phenoxymethylvinylidene-benzofuran (3b). A mixture of aminal **1b** (2.8 g, 10 mmoles), phenyl propargyl ether (1.5 mL, 12 mmoles), and CuI (1.9 g, 10 mmoles) was boiled for 30 min in MeCN (10 mL), cooled, and then concentrated NH_4OH (25 mL) and water (80 mL) were added. The oil that separated crystallized when held in a refrigerator over several days. The solid material was dissolved in $CHCl_3$ and passed through a column packed with Al_2O_3, the solvent was evaporated, and the residue was recrystallized from MeOH, and dried *in vacuo*. The yield of **3b** was 1 g (31 %), m.p. 72—73 °C. Found (%): C, 74.59; H, 6.41; N, 4.31. $C_{20}H_{21}NO_3$. Calculated (%): C, 74.30; H, 6.50; N, 4.33. IR, ν/cm^{-1}: 1694 (C=C), 755, 690 (the monosubstituted benzene ring). The ^{1}H NMR ($CDCl_3$, δ): 2.50 (m, 2 H, CH_2N); 2.62 (m, 2 H, CH_2N); 3.65 (m, 4 H, CH_2O, morpholine); 4.85 (m, 3 H, CH_2O, CHN); 5.22 (t, 1 H, CH); 6.90—7.05 (m, 5 H, arom.).

2-Benzylidene-3-morpholino-5-nitro-3*H*-benzofuran (3c). A mixture of morpholinal **1c** (3.2 g, 10 mmoles), CuI (1.7 g, 10 mmoles), and phenylacetylene (1.1 mL, 10 mmoles) was boiled with stirring in MeCN (10 mL) for 30 min, cooled, and then concentrated NH_4OH (5 mL) and water (20 mL) were added. The sticky precipitate, which crystallized on trituration, was filtered off, extracted with boiling heptane, and the precipitate (0.5 g) obtained after evaporation was recrystallized from ethyl acetate. An additional amount of **3c** (1.15 g) was obtained by extraction with boiling heptane. The total yield of **3c** was 1.65 g (48.8 %), it was a yellow material, m.p. 149—155 °C. Found (%): C, 67.05; H, 5.58; N, 7.85. $C_{19}H_{18}N_2O_4$. Calculated (%): C, 67.46; H, 5.33; N, 8.28. IR, ν/cm^{-1}: 1687 (C=C), 1614, 1601, 1580 (arom.), 1514, 1327 (NO_2). The ^{1}H NMR ($CDCl_3$, δ): 2.55 (m, 2 H, CH_2N); 2.76 (m, 2 H, CH_2N); 3.68 (t, 4 H, CH_2O); 5.07 (s, 1 H, CH); 5.98 (s, 1 H, =CH—); 7.12 (d, 1 H, C(7)—H, arom.); 7.12—7.72 (m, 5 H, Ph); 8.25 (dd, 1 H, C(6)—H, arom.); 8.32 (d, 1 H, C(4)—H, arom.).

When a solution of **3c** in acetic acid was treated with an excess of the 57 % $HClO_4$ solution at ~20 °C, the respective perchlorate was obtained in a quantitative yield; the perchlorate after precipitation with ether and recrystallization from MeOH contained 0.5 solvate MeOH molecule, its m.p. was 140—145 °C.

2-Dimethylhydroxymethylvinylidene-3-morpholino-5-nitro-benzo-3*H*-furan (3d). A mixture of aminal **1c** (1.6 g, 5 mmoles) and dimethylethynylcarbinol (1 mL, 10 mmoles) was heated

Table 1. Principal crystallographic parameters for **2b*** and **3c** · $HClO_4$**

Parameter	**2b**	Perchlorate **3c**
a/Å	9.274(2)	24.604(2)
b/Å	18.353(3)	8.856(3)
c/Å	9.382(4)	19.341(4)
V/Å^3	1582.4(1.3)	4191.6(2.8)
d_{calc}/g cm^{-3}	1.227	1.499
β/deg	97.71(2)	95.94(2)
Sp. group	$P2_1/c$	$C2/c$
Z	4	8

* At −95 °C. ** At 20 °C.

Table 2. Fractional atomic coordinates for nonhydrogen atoms (×10^4) and their temperature factors (Å^2, ×10^3) in **2b**

Atom	*x*	*y*	*z*	U_{eq}
O(1)	1375(2)	8560(1)	605(2)	47(1)
C(1)	1849(3)	9230(1)	1117(3)	33(1)
C(2)	921(3)	9708(1)	1715(2)	31(1)
C(3)	1473(3)	10379(1)	2238(3)	35(1)
C(4)	2891(4)	10572(2)	2128(3)	42(1)
C(5)	3789(4)	10107(2)	1498(3)	43(1)
C(6)	3269(3)	9433(2)	995(3)	38(1)
C(7)	−655(3)	9477(1)	1743(3)	31(1)
C(8)	−1524(3)	10013(1)	2419(3)	35(1)
C(9)	−2235(3)	10450(1)	2964(3)	36(1)
C(11)	−3073(3)	11000(1)	3582(3)	33(1)
C(12)	−3753(3)	10845(2)	4779(3)	41(1)
C(13)	−4538(4)	11384(2)	5372(3)	53(1)
C(14)	−4629(4)	12071(2)	4797(3)	57(1)
C(15)	−3950(4)	12230(2)	3613(3)	51(1)
C(16)	−3177(3)	11700(2)	2989(3)	40(1)
N(21)	−700(2)	8734(1)	2371(2)	32(1)
C(22)	−145(4)	8725(2)	3908(3)	40(1)
C(23)	−130(4)	7952(2)	4468(4)	50(1)
O(24)	−1557(2)	7650(1)	4263(2)	49(1)
C(25)	−2111(4)	7655(2)	2763(3)	49(1)
C(26)	−2160(3)	8415(2)	2146(3)	41(1)

Table 3. Fractional atomic coordinates for hydrogen atoms ($\times10^3$) and their temperature factors (Å^2, $\times10^2$) in **2b**

Atom	x	y	z	U_{eq}
H(1(O))	51(5)	847(2)	119(5)	9(1)
H(3a)	85(3)	1070(2)	266(3)	4(1)
H(4a)	322(3)	1107(2)	246(3)	6(1)
H(5a)	481(3)	1022(1)	141(3)	3(1)
H(6a)	383(3)	910(2)	58(3)	4(1)
H(7a)	−105(3)	942(1)	82(3)	3(1)
H(12a)	−371(3)	1039(2)	517(3)	3(1)
H(13a)	−507(4)	1128(2)	618(4)	6(1)
H(14a)	−509(3)	1244(2)	521(3)	5(1)
H(15a)	−396(3)	1273(2)	325(3)	5(1)
H(16a)	−267(4)	1180(2)	218(4)	6(1)
H(22a)	−75(4)	903(2)	450(3)	5(1)
H(22b)	89(4)	892(2)	407(3)	6(1)
H(23a)	19(3)	795(2)	554(4)	5(1)
H(23b)	52(4)	767(2)	385(4)	5(1)
H(25a)	−306(4)	744(2)	275(3)	5(1)
H(25b)	−141(4)	734(2)	221(4)	8(1)
H(26a)	−252(3)	843(1)	110(3)	4(1)
H(26b)	−285(4)	873(2)	264(3)	5(1)

Table 4. Bond lengths in **2b**

Bond	d/Å	Bond	d/Å
O(1)—C(1)	1.372(3)	C(11)—C(12)	1.389(4)
C(1)—C(2)	1.398(4)	C(11)—C(16)	1.399(4)
C(1)—C(6)	1.388(4)	C(12)—C(13)	1.387(5)
C(2)—C(3)	1.396(4)	C(13)—C(14)	1.370(5)
C(2)—C(7)	1.526(4)	C(14)—C(15)	1.379(5)
C(3)—C(4)	1.379(5)	C(15)—C(16)	1.384(5)
C(4)—C(5)	1.379(5)	N(21)—C(22)	1.464(3)
C(5)—C(6)	1.388(4)	N(21)—C(26)	1.464(4)
C(7)—C(8)	1.469(4)	C(22)—C(23)	1.511(4)
C(7)—N(21)	1.489(3)	C(23)—O(24)	1.425(4)
C(8)—C(9)	1.196(4)	O(24)—C(25)	1.432(4)
C(9)—C(11)	1.442(4)	C(25)—C(26)	1.508(4)

to boiling in MeCN (15 mL). CuI (0.5 g, 2.5 mmoles) was added, and then the mixture was boiled for 30 min. Concentrated NH_4OH (20 mL) and ice water (80 mL) were added to the cooled reaction mixture, and the mixture was stirred with a stirring rod and held in a refrigerator during several hours. The obtained precipitate was filtered off, washed with diluted NH_4OH and water, dried on a filter, and recrystallized from octane. The yield of **3d** was 0.71 g (44.7 %), m.p. 114—115 °C. Found (%): C, 59.43; H, 5.84; N, 8.40. $C_{16}H_{20}N_2O_5$. Calculated (%): C, 60.00; H, 6.25; N, 8.75. IR, ν/cm^{-1}: 3380, 3320 (OH), 1694 (C=C), 1621, 1601 (arom.), 1527, 1341 (NO_2). The ^1H NMR ($CDCl_3$, δ): 1.56 (s, 6 H, CH_3); 2.60 (m, 4 H, CH_2N); 3.72 (t, 4 H, CH_2O); 4.90 (s, 1 H, CH); 5.30 (s, 1 H, =CH); 7.00 (d, 1 H, arom.); 8.20 (d, 2 H, arom.).

2-Dimethylhydroxymethylvinylidene-3-piperidino-3*H*-benzofuran (3e). A mixture of aminal **1a** (2.74 g, 10 mmoles) and dimethylethynylcarbinol (1 mL, 10 mmoles) was heated to boiling in MeCN (15 mL). CuI (1.9 g, 10 mmoles) was added, the mixture was boiled for 30 min, filtered off in a hot state, and the precipitate was washed on a filter with MeCN. Then concentrated NH_4OH (20 mL) and ice water (40 mL) were added to the cooled filtrate. After being cooled with ice and triturated with a stick, the oil obtained was crystallized out. After recrystallization from octane, 1 g of compound **3e** (36.6 %) was obtained, m.p. 99—102 °C (from hexane). Found (%): C, 74.45; H, 8.05; N, 4.72. $C_{17}H_{23}NO_2$. Calculated (%):

Table 5. Bond angles in **2b**

Angle	ω/deg	Angle	ω/deg
O(1)—C(1)—C(2)	121.2(3)	C(9)—C(11)—C(16)	119.6(2)
O(1)—C(1)—C(6)	118.3(2)	C(12)—C(11)—C(16)	119.7(3)
C(2)—C(1)—C(6)	120.5(2)	C(11)—C(12)—C(13)	119.9(3)
C(1)—C(2)—C(3)	118.5(3)	C(12)—C(13)—C(14)	120.4(3)
C(1)—C(2)—C(7)	118.4(2)	C(13)—C(14)—C(15)	120.1(3)
C(3)—C(2)—C(7)	123.1(2)	C(14)—C(15)—C(16)	120.7(3)
C(2)—C(3)—C(4)	120.6(3)	C(11)—C(16)—C(15)	119.3(3)
C(3)—C(4)—C(5)	120.7(3)	C(7)—N(21)—C(22)	112.0(2)
C(4)—C(5)—C(6)	119.7(3)	C(7)—N(21)—C(26)	112.6(2)
C(1)—C(6)—C(5)	120.0(3)	C(22)—N(21)—C(26)	109.5(2)
C(2)—C(7)—C(8)	113.8(2)	N(21)—C(22)—C923)	109.8(2)
C(2)—C(7)—N(21)	109.8(2)	C(22)—C(23)—O(24)	110.7(3)
C(8)—C(7)—N(21)	113.4(2)	C(23)—O(24)—C(25)	109.5(3)
C(7)—C(8)—C(9)	179.8(3)	O(24)—C(25)—C(26)	111.8(2)
C(8)—C(9)—C(11)	177.7(3)	N(21)—C(26)—C(25)	109.5(2)
C(9)—C(11)—C(12)	120.7(2)		

Table 6. Fractional atomic coordinates for nonhydrogen atoms ($\times10^4$) and their temperature factors (Å^2, $\times10^3$) in **3c** · $HClO_4$

Atom	x	y	z	U_{eq}
Cl(1)	1081(1)	11140(3)	9261(2)	64(1)
O(1)	1188(6)	10671(11)	9951(5)	123(6)
O(2)	561(5)	11836(13)	9204(6)	116(5)
O(3)	1464(5)	12219(12)	9063(7)	124(6)
O(4)	1067(4)	9844(9)	8816(4)	70(3)
O(5)	1255(4)	3099(13)	12459(5)	89(4)
O(6)	874(4)	5273(11)	12304(4)	71(4)
O(4')	−164(3)	5973(10)	9001(4)	65(3)
O(1c)	2161(3)	5227(8)	9742(4)	26(2)
N(2)	1168(4)	4275(14)	12129(5)	53(4)
N(1')	923(3)	6956(10)	9452(5)	40(3)
C(2)	1937(4)	6575(12)	9485(5)	38(4)
C(3)	1470(4)	7015(12)	9913(5)	36(4)
C(4)	1510(4)	5859(11)	10454(5)	35(4)
C(5)	1264(4)	5683(12)	11066(6)	36(4)
C(6)	1426(4)	4450(14)	11476(5)	46(4)
C(7)	1816(5)	3461(13)	1333(7)	54(5)
C(8)	2080(5)	3668(15)	10743(8)	57(5)
C(9)	1932(4)	4859(12)	10334(5)	44(4)
C(10)	2113(4)	7335(12)	8951(6)	46(4)
C(11)	2547(4)	6976(12)	8532(6)	44(4)
C(12)	2922(4)	5811(12)	8679(6)	44(4)
C(13)	3345(6)	5570(15)	8267(9)	69(6)
C(14)	3368(5)	6467(18)	7679(9)	74(6)
C(15)	3003(6)	7559(19)	7511(7)	69(6)
C(16)	2588(5)	7856(14)	7937(6)	51(5)
C(2')	818(4)	5494(12)	9072(6)	44(4)
C(3')	280(5)	5573(17)	8613(7)	61(5)
C(5')	−73(5)	7382(18)	9302(8)	64(6)
C(6')	440(4)	7380(14)	9832(7)	51(4)
O(1s)	183(19)	9739(53)	7477(38)	129(19)
C(1s)	−83(31)	10961(66)	7663(37)	87(21)

Table 7. Fractional atomic coordinates for hydrogen atoms ($\times 10^3$) and their temperature factors (Å^2, $\times 10^2$) in **3c** · $HClO_4$

Atom	*x*	*y*	*z*
H(1N')	98(4)	776(12)	927(6)
H(3)	149(4)	805(12)	1011(5)
H(5)	101(4)	633(11)	1119(5)
H(7)	187(4)	264(12)	1164(5)
H(8)	226(5)	315(13)	1064(7)
H(10)	190(4)	837(11)	876(5)
H(12)	292(4)	502(11)	920(5)
H(13)	352(4)	467(12)	848(5)
H(14)	366(4)	608(12)	752(5)
H(15)	302(4)	830(11)	716(6)
H(16)	236(4)	879(12)	793(5)
H(2a')	110(4)	507(11)	876(5)
H(2b')	82(4)	471(11)	959(5)
H(3a')	28(4)	618(12)	824(6)
H(3b')	17(4)	449(11)	840(5)
H(5a')	−5(4)	820(12)	899(6)
H(5b')	−37(4)	773(11)	948(5)
H(6a')	52(4)	836(11)	1009(5)
H(6b')	41(4)	646(11)	1027(5)

Note. For all atoms, the fixed temperature factor of $5 \cdot 10^{-2}$ Å^2 was used.

Table 8. Bond lengths in **3c** · $HClO_4$

Bond	*d*/Å	Bond	*d*/Å
Cl(1)—O(1)	1.40(1)	C(4)—C(5)	1.39(2)
Cl(1)—O(2)	1.41(1)	C(4)—C(9)	1.40(2)
Cl(1)—O(3)	1.42(1)	C(5)—C(6)	1.38(2)
Cl(1)—O(4)	1.433(9)	C(6)—C(7)	1.35(2)
O(5)—N(2)	1.23(2)	C(7)—C(8)	1.38(2)
O(6)—N(2)	1.21(1)	C(8)—C(9)	1.35(2)
O(4')—C(3')	1.43(2)	C(10)—C(11)	1.44(2)
O(4')—C(5')	1.39(2)	C(11)—C(12)	1.39(1)
O(1c)—C(2)	1.38(1)	C(11)—C(16)	1.40(2)
O(1c)—C(9)	1.37(1)	C(12)—C(13)	1.39(2)
C(2)—C(6)	1.48(2)	C(13)—C(14)	1.39(2)
N(1')—C(3)	1.53(1)	C(14)—C(15)	1.34(2)
N(1')—C(2')	1.50(1)	C(15)—C(16)	1.40(2)
N(1')—C(6')	1.51(2)	C(2')—C(3')	1.52(2)
C(2)—C(3)	1.53(1)	C(5')—C(6')	1.54(2)
C(2)—C(10)	1.34(2)	O(1s)—C(1s)	1.33(8)
C(3)—C(4)	1.46(1)		

Table 9. Bond angles in **3c** · $HClO_4$

Angle	ω/deg
O(1)—Cl(1)—O(2)	106.4(8)
O(1)—Cl(1)—O(3)	113.2(8)
O(2)—Cl(1)—O(3)	107.8(7)
O(1)—Cl(1)—O(4)	109.0(6)
O(2)—Cl(1)—O(4)	109.7(6)
O(3)—Cl(1)—O(4)	110.6(7)
C(3')—O(4')—C(5')	110.1(10)
C(2)—O(1c)—C(9)	108.9(8)
O(5)—N(2)—O(6)	123.4(10)
O(5)—N(2)—C(6)	117.7(10)
O(6)—N(2)—C(6)	118.9(10)
C(3)—N(1')—C(2')	114.3(8)
C(3)—N(1')—C(6')	113.3(8)
C(2')—N(1')—C(6')	110.5(8)
O(1c)—C(2)—C(3)	108.5(8)
O(1c)—C(2)—C(10)	124.1(9)
C(3)—C(2)—C(10)	127.4(9)
N(1')—C(3)—C(2)	109.7(8)
N(1')—C(3)—C(4)	112.5(8)
C(2)—C(3)—C(4)	102.1(8)
C(3)—C(4)—C(5)	133.1(9)
C(3)—C(4)—C(9)	108.8(9)
C(5)—C(4)—C(9)	117.7(9)
C(4)—C(5)—C(6)	116.7(9)
N(2)—C(6)—C(5)	116.6(10)
N(2)—C(6)—C(7)	119.0(10)
C(5)—C(6)—C(7)	124.4(11)
C(6)—C(7)—C(8)	119.2(11)
C(7)—C(8)—C(9)	117.8(12)
O(1c)—C(9)—C(4)	111.3(9)
O(1c)—C(9)—C(8)	124.7(11)
C(4)—C(9)—C(8)	124.0(11)
C(2)—C(10)—C(11)	129.7(10)
C(10)—C(11)—C(12)	124.2(11)
C(10)—C(11)—C(16)	117.4(10)
C(12)—C(11)—C(16)	118.4(11)
C(11)—C(12)—C(13)	121.0(11)
C(12)—C(13)—C(14)	118.3(12)
C(13)—C(14)—C(15)	121.9(15)
C(14)—C(15)—C(16)	120.3(14)
C(11)—C(16)—C(15)	119.8(11)
N(1')—C(2')—C(3')	110.1(9)
O(4')—C(3')—C(2')	111.7(10)
O(4')—C(5')—C(6')	111.4(11)
N(1')—C(6')—C(5')	108.0(10)

C, 74.73; H, 8.42; N, 5.13. IR, ν/cm^{-1}: 3333 (OH), 1694 (C=C), 1607, 1601 (arom.). The ^{1}H NMR ($CDCl_3$, δ): 1.56 (m, 12 H, CH_2 + CH_3); 2.55 (m, 4 H, CH_2N); 4.80 (s, 1 H, CH); 5.15 (s, 1 H, =CH); 6.80—7.40 (m, 4 H, arom.).

X-ray diffraction study of compound 2b and perchlorate of 3c. The principal crystallographic parameters for structures **2b** and **3c** · $HClO_4$ are given in Table 1.

The unit-cell parameters and intensities of reflections were measured on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scan technique); for **2b**: $T = -95$ °C, $\theta_{max} = 27°$; for **3c** perchlorate: $T = 20$ °C, $\theta_{max} = 28°$.

The structures were solved by the full-matrix least-squares method with anisotropic thermal parameters for the nonhydrogen atoms. Hydrogen atoms, the initial positions of which were calculated (except for the hydroxyl hydrogen atom in **2b**, which was located from a difference Fourier synthesis), were refined isotropically by the least-squares method. The difference Fourier synthesis revealed the solvate MeOH molecule, which was disordered over two sites related by a twofold axis, with the overall occupancy of 0.5. The final reliability factors for **2b** were $R = 0.044$, $R_w = 0.076$ using 1684 independent reflections with $I > 2.5\sigma$; for **3c** · $HClO_4$ $R = 0.098$, $R_w = 0.099$ using 1677 independent reflections with $I > 2.5$ s.

All calculations were performed on an IBM PC/AT-286 computer using the SHELXTL program package. Atomic coordinates and temperature factors for **2b** are given in Tables 2 and 3, geometric parameters for the molecule are listed in Tables 4 and 5; data on perchlorate **3c** are given in Tables 6, 7, 8, and 9, respectively.

References

1. V. N. Komissarov, L. Yu. Ukhin, Zh. I. Orlova, and O. A. Tokarskaya, *Zh. Org. Khim.*, 1987, **23**, 1325 [*J. Org. Chem. USSR*, 1987, **23** (Engl. Transl.)].
2. V. N. Komissarov and L. Yu. Ukhin, *Zh. Org. Khim.*, 1989, **25**, 2594 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
3. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
4. R. S. Drago, *Physical Methods in Inorganic Chemistry*, Reinhold, New York, Chapman, London, 1965.
5. A. V. Koblik, K. F. Suzdalev, and G. N. Dorofeenko, *Khim. Geterotsikl. Soedin.*, 1982, **2**, 163 [*Chem. Heterocycl. Compd.*, 1982, **2** (Engl. Transl.)].
6. K. F. Suzdalev and A. V. Koblik, *Khim. Geterotsikl. Soedin.*, 1989, **3**, 313 [*Chem. Heterocycl. Compd.*, 1989, **3** (Engl. Transl.)].

Received July 7, 1993