Reaction of 6-methoxybenzo[*b*]furan-3(2*H*)-one and benzo[*b*]thiophen-3(2*H*)-one with 2-aryl-1,1-dicyanoethylenes as a convenient synthetic route to substituted 2-amino-4-aryl-1,3-dicyano-7-methoxydibenzo[*b*,*d*]furans and 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans

A. M. Shestopalov* and O. A. Naumov

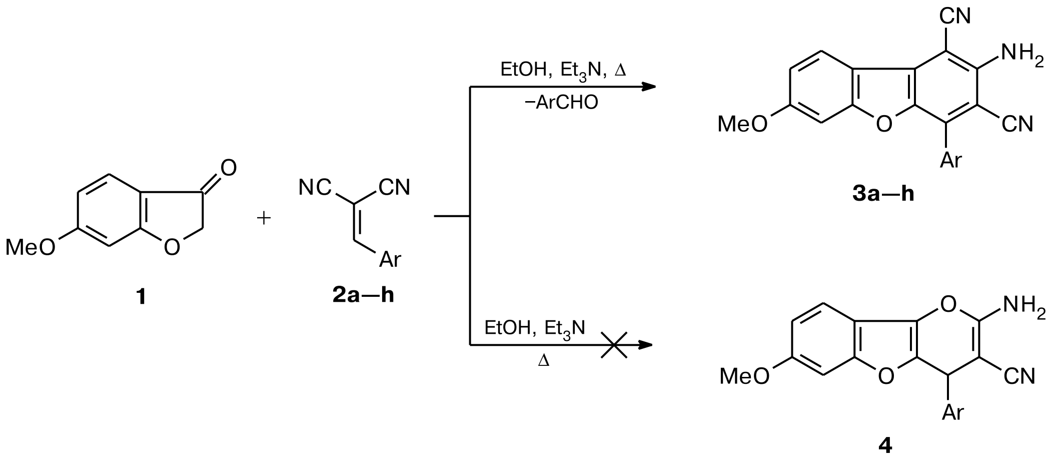
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: shchem@dol.ru

The reactions of 6-methoxybenzo[*b*]furan-3(2*H*)-one with 2-aryl-1,1-dicyanoethylenes and malononitrile or with aromatic aldehyde and two moles of malononitrile afford 2-amino-4-aryl-1,3-dicyano-7-methoxydibenzo[*b*,*d*]furans. The reactions of benzo[*b*]thiophen-3(2*H*)-one with 2-aryl-1,1-dicyanoethylenes or with aromatic aldehyde and one mole of malononitrile produce 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans.

Key words: 6-methoxybenzo[*b*]furan-3(2*H*)-one, 6-methoxy-2-[(4-aryl)methylidene]-1-benzofuran-3(2*H*)-one, 2-amino-4-aryl-1,3-dicyano-7-methoxydibenzo[*b*,*d*]furan, benzo[*b*]thiophen-3(2*H*)-one, 2-[(4-aryl)methylidene]-1-benzothiophen-3(2*H*)-one, 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyran, three-component condensation.

The reactions of 1-acetyl-1,2-dihydroindol-3(2*H*)-one with 2-aryl(hetaryl)-1,1-dicyanoethylenes have previously been shown[1,2] to afford 5-acetyl-2-amino-4-aryl-3-cyano-4,5-dihydropyrano[3,2-*b*]indoles. The method of one-pot synthesis of substituted pyrano[3,2-*b*]indoles (without preliminary preparation and isolation of unsaturated nitriles) by the three-component condensation of 1-acetylindol-3(2*H*)-one, aromatic aldehyde, and malononitrile was developed.[3] In continuation of the studies of heterocyclic ketones with 2-aryl(hetaryl)-1,1-dicyanoethylenes, we studied the reaction of 6-methoxybenzo[*b*]furan-3(2*H*)-one (**1**), which is the oxygen analog of 3-oxoindole, with arylmethylidenemalononitriles **2a—h**. It turned out that this reaction afforded 2-amino-4-aryl-1,3-dicyano-7-methoxydibenzo[*b*,*d*]furans **3a—h** instead of the expected 2-amino-4-aryl(hetaryl)-3-cyano-7-methoxy-4*H*-pyran[3,2-*b*]benzofurans **4** (method *A*, Scheme 1).

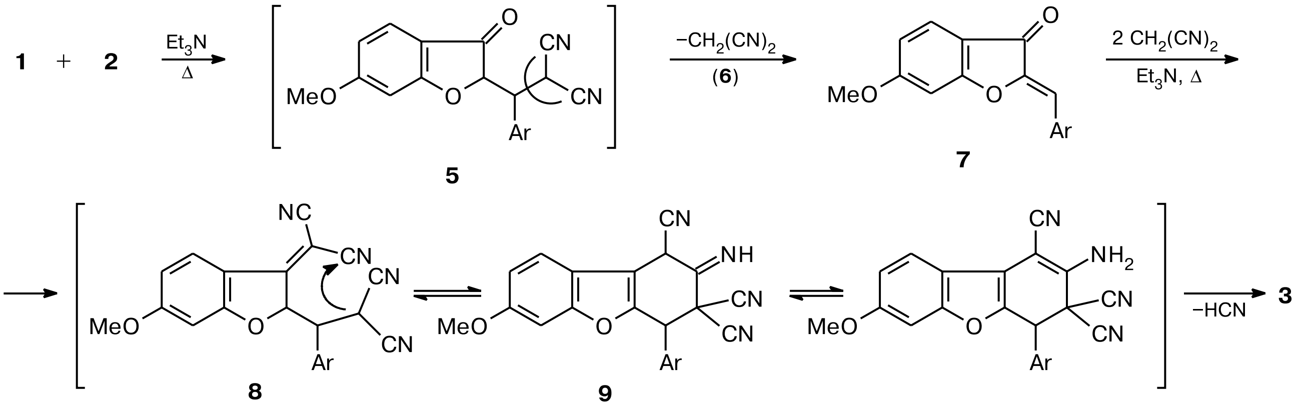
Scheme 1



2, 3	a	b	c	d	e	f	g	h
Ar	Ph	4-FC$_6$H$_4$	2-ClC$_6$H$_4$	4-ClC$_6$H$_4$	2-BrC$_6$H$_4$	3-BrC$_6$H$_4$	3-py	3-Thienyl

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 911—917, April, 2003.

Scheme 2



Primarily formed Michael adducts **5** undergo 1,2-elimination of a molecule of malononitrile **6** to form 2-[(4-aryl)methylidene]-6-methoxy-1-benzofuran-3(2*H*)-ones **7** (Scheme 2). Compounds **7a—c** were isolated and characterized (Tables 1 and 2). The reaction of malononitrile **6** (2 mol) with intermediate **7** affords adduct **8**, which undergoes ring closure *via* the Thorpe—Ziegler reaction to form imine **9**. The subsequent tautomeric transformation and dehydrocyanation afford benzofuran **3**. The reaction mixture also contains compounds **7a,b** (Ar = 4-FC_6H_4 (**a**), 4-ClC_6H_4 (**b**)), which were isolated.

Aromatic aldehyde ArCHO **10** is formed in the reactions of benzofuranone **1** with arylmethylidenemalononitriles **2i,j** (Ar = 2-FC_6H_4 (**i**), 4-BrC_6H_4 (**j**)), indicating the different reaction course (Scheme 3).

It is known[5] that the condensation of malononitrile **6** and aromatic aldehydes **10** (Knoevenagel reaction) is reversible. Therefore, the reaction mixture (a solution in 96% EtOH) can contain both compounds **1**, **2** and compounds **6**, **10**. Probably, malononitrile **6** is condensed with 6-methoxybenzofuran-3(2*H*)-one (**1**) to form unsaturated dinitrile **11**, which reacts with arylmethylidenemalononitrile **2** in the Michael reaction. The further

Table 1. Physicochemical characteristics of compounds **7a—c**

Compound 7	Ar	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	Molecular formula	MS, *m/z* ($[M]^+$)
a	4-FC_6H_4	76	173—175	70.81 71.11	3.98 4.10	$C_{16}H_{11}FO_3$	270
b	4-ClC_6H_4	87	166—168	66.85 67.03	3.54 3.87	$C_{16}H_{11}ClO_3$	286
c	2-Thienyl	73	187—189	65.24 65.10	4.05 3.90	$C_{14}H_{10}O_2S$	258

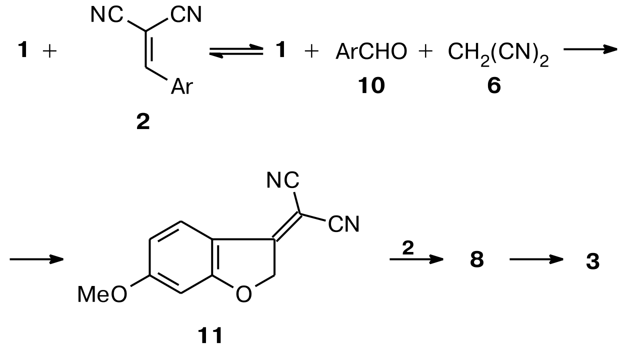
Table 2. Spectroscopic characteristics of compounds **7a—c***

Compound 7	^1H NMR, δ (*J*/Hz)					IR, ν(CO)/cm^{-1}
	OCH_3 (s, 3 H)	H(5), H(7) (m, 2 H)	—CH= (s, 1 H)	H(4) (d, 1 H)	Ar	
a	3.90	6.80—6.90	7.10	7.69 (*J* = 1.3)	7.31 (t, 2 H, H(6´), H(2´), *J* = 8.8); 8.01 (t, 2 H, H(5´), H(3´), *J* = 8.8)	1710
b	3.95	6.80—6.90	7.10	7.70 (*J* = 1.3)	7.55 (d, 2 H, H(6´), H(2´), *J* = 8.4); 7.98 (d, 2 H, H(5´), H(3´), *J* = 8.4)	1703
c	3.94	6.80—6.90	—**	7.80 (*J* = 1.1)	7.11—7.20 (m, 2 H, 2-CH=, Ar); 7.60—7.65 (m, 2 H, Ar)	1696

* The signals were assigned according to the experimental data.[4]

** Superimposed on the signals of the substituent.

Scheme 3



transformation of intermediate **8** into dibenzofuran **3** proceeds similarly to Scheme 1. In this case, aromatic aldehydes **10** remain in excess. They were isolated in the pure state or characterized as arylmethylidenemalononitriles **2i,j** due to the addition of malononitrile **6** to the filtrate.

The scheme of the reaction can be attributed, most likely, to the Bell—Evans—Polanyi (BEP) rules, which were presented for the pair of carbonyl compounds: cyclohexanone and benzaldehyde in the reaction with thiosemicarbazide.[6] Since arylmethylidenemalononitrile **2**, like benzaldehyde thiosemicarbazone, in protic solvents exists in the kinetic equilibrium with the initial compounds, we can assume that arylmethylidenemalononitrile **2** is thermodynamically unstable and is formed *via* the kinetically controlled reaction route. By analogy between cyclohexanone thiosemicarbazone and intermediate **11** (although it does not completely correspond to cyclohexanone thiosemicarbazone because has the annelated aromatic cycle), it can be assumed that compound **11** is thermodynamically stable and its reaction is thermodynamically controlled and irreversible. Therefore, the reactions of benzofuranone **1** with arylmethylidenemalononitriles **2** afford aromatic aldehydes. In both cases (see Schemes 2 and 3), the reactions are accompanied by the elimination of HCN, are irreversible, and afford dibenzofurans **3**.

We mentioned that the direction of the process is affected by the nature of a substituent in arylmethylidenemalononitrile **2**. For example, unsubstituted benzylidenemalononitrile **2a** and arylmethylidenemalononitriles containing electron-withdrawing substituents, such as the nitro group (compound **2l**) and halogen atoms (compounds **2b—f,i,j,l,o** and heterocyclic derivatives **2g,h,p,q**), readily enter into this reaction. Arylmethylidenemalononitriles **2** containing electron-releasing substituents (one or two alkoxy groups, dialkylamino groups) do not react.

The experimental results were used to develop simpler methods for the synthesis of substituted dibenzofurans **3**. Taking into account Scheme 2, we purposefully obtained compounds **3** by the step-by-step synthesis with preliminary isolation of intermediate **7** followed by its reaction with malononitrile **6** (2 mol) in EtOH (method *B*, Scheme 4).

Scheme 4

Ar = 4-FC_6H_4 (**3b, 7a**), 4-ClC_6H_4 (**3d, 7b**)

Since the Michael adducts **8** are generated in the reaction with arylmethylidenemalononitrile **2**, it is reasonable to assume that 2-amino-3-cyanodibenzofurans **3** can be synthesized without preliminary synthesis of 2-arylmethylidene-6-methoxy-1-benzofuran-3(2*H*)-one **7** or arylmethylidenemalononitriles **2** by the three-component condensation of 6-methoxybenzo[*b*]furan-3(2*H*)-one (**1**), the corresponding aldehyde **10**, and malononitrile **6**. Indeed, the reaction of 6-methoxybenzo[*b*]furan-3(2*H*)-one (**1**) with malononitrile **6** (2 mol) and aldehyde **10** (1 mol) in EtOH in the presence of Et_3N affords dibenzofurans **3** (method *C*, Scheme 5) in approximately the same yields as in method *A* (Tables 3 and 4).

Scheme 5

3, 10: Ar = 4-FC_6H_4 (**3b, 10a**), 2-ClC_6H_4 (**3c, 10b**), 4-ClC_6H_4 (**3d, 10c**), 3-py (**3g, 10d**), 2-FC_6H_4 (**3i, 10e**), 4-BrC_6H_4 (**3j, 10f**), 3-$NO_2C_6H_4$ (**3k, 10g**), 3-FC_6H_4 (**3l, 10h**), 2-$CF_3C_6H_4$ (**3m, 10i**), 2,3-$Cl_2C_6H_3$ (**3n, 10j**), 2-F-5-BrC_6H_3 (**3o, 10k**), 4-py (**3p, 10l**), 2-thienyl (**3q, 10m**), 4-$MeOOCC_6H_4$ (**3r, 10n**)

Unlike 6-methoxybenzo[*b*]furan-3(2*H*)-one (**1**), the reactions of benzo[*b*]thiophen-3(2*H*)-one (**12**) with arylmethylidenemalononitriles **2a,b,l** under similar conditions (heating of equimolar amounts of compounds **12** and **2** in EtOH in the presence of Et_3N) occur differently and afford 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans **13a—c** (method *A*, Scheme 6) in high yields (Tables 5 and 6).

The scheme of this reaction can include transformations similar to those described previously[3] for the reactions of 1-acetylindol-3(2*H*)-one with 2-aryl(hetaryl)-1,1-dicyanoethylenes **2**: Michael adduct **14** is primarily formed and then undergoes intramolecular ring closure to form aminopyran **13**.

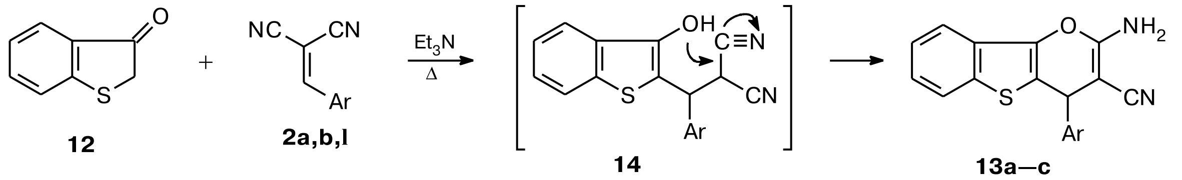
According to the scheme described above, 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans **13b,c** were prepared by the step-by-step synthesis with preliminary isolation of the corresponding 2-arylmethylidene-1-benzothiophen-3(2*H*)-one **15a,b** (Tables 7 and 8) followed by its reaction with malononitrile **6** in EtOH (method *B*, Scheme 7).

Table 3. Physicochemical characteristics of compounds **3a—r**

Compound **3**	Ar	Yield (%) (method)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula	MS, *m/z* ([M]$^+$)
a	C_6H_5	42 (*A*)	293—295	74.69 74.34	3.55 3.83	12.74 12.39	$C_{21}H_{12}N_3O_2$	339
b	4-FC_6H_4	34 (*A*), 51 (*B*), 43 (*C*)	275—277	70.29 70.59	3.22 3.36	12.50 12.11	$C_{21}H_{12}FN_3O_2$	357
c	2-ClC_6H_4	36 (*A*), 31 (*C*)	248—250	67.82 67.47	2.93 3.21	11.59 11.24	$C_{21}H_{12}ClN_3O_2$	374
d	4-ClC_6H_4	46 (*A*), 36 (*B*), 42(*C*)	308—310	67.77 67.47	3.49 3.21	11.64 11.24	$C_{21}H_{12}ClN_3O_2$	374
e	2-BrC_6H_4	42 (*A*)	318—320	59.94 60.29	2.59 2.87	9.70 10.05	$C_{21}H_{12}BrN_3O_2$	418
f	3-BrC_6H_4	47 (*A*)	266—268	60.64 60.29	3.15 2.87	10.40 10.05	$C_{21}H_{12}BrN_3O_2$	418
g	3-py	47 (*A*), 41 (*C*)	318—320	70.94 70.59	3.81 3.53	16.12 16.47	$C_{20}H_{12}N_4O_2$	340
h	3-Thienyl	40 (*A*)	292—294	66.44 66.09	2.91 3.19	12.52 12.17	$C_{19}H_{11}N_3O_2S$	345
i	2-FC_6H_4	46 (*C*)	245—247	70.24 70.59	3.64 3.36	11.36 11.76	$C_{21}H_{12}FN_3O_2$	357
j	4-BrC_6H_4	47 (*C*)	305—307	59.99 60.29	2.73 2.87	9.65 10.05	$C_{21}H_{12}BrN_3O_2$	418
k	3-$NO_2C_6H_4$	51 (*C*)	207—209	65.28 65.63	2.99 3.13	14.23 14.58	$C_{21}H_{12}N_4O_4$	384
l	3-FC_6H_4	39 (*C*)	287—289	70.94 70.59	3.08 3.36	11.76 11.76	$C_{21}H_{12}FN_3O_2$	357
m	2-$CF_3C_6H_4$	41 (*C*)	270—272	65.21 64.86	3.23 2.95	10.72 10.32	$C_{22}H_{12}F_3N_3O_2$	407
n	2,3-$Cl_2C_6H_3$	32 (*C*)	276—278	61.62 60.92	2.99 2.70	10.67 10.32	$C_{21}H_{11}Cl_2N_3O_2$	407
o	2-F-5-BrC_6H_3	56 (*C*)	258—260	58.15 57.80	2.24 2.52	9.98 9.63	$C_{21}H_{11}FBrN_3O_2$	436
p	4-py	49 (*C*)	304—306	70.24 70.59	3.39 3.53	16.07 16.47	$C_{20}H_{12}N_4O_2$	340
q	2-Thienyl	56 (*B*), 54 (*C*)	263—265	65.74 66.09	3.47 3.19	11.82 12.17	$C_{19}H_{11}N_3O_2S$	345
r	4-$MeOOCC_6H_4$	43 (*C*)	313—315	69.24 69.52	3.98 3.78	10.93 10.58	$C_{23}H_{15}N_3O_4$	397

Since the Michael adducts **15** are generated in the reaction with arylmethylidenemalononitrile **2**, it seems reasonable that 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans **13** can be prepared by a simpler method, *viz.*, in one step, without preliminary synthesis of 2-arylmethylidene-1-benzothiophen-3(2*H*)-one **15** or

Scheme 6

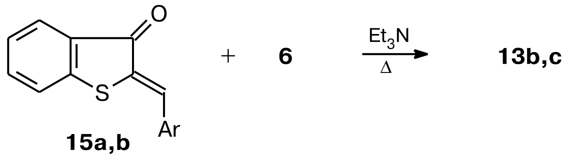


13: Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**)

Table 4. Spectroscopic characteristics of compounds **3a—r**

Compound 3	^{1}H NMR, δ (*J*/Hz)			IR, ν/cm^{-1}		
	OCH$_3$	NH$_2$	Ar	δ(NH$_2$)	ν(CN)	ν(NH$_2$)
a	3.88 (m, 3 H)	6.41 (br.s, 2 H)	7.04, 7.20 (both s, 1 H each, Ar); 7.60—7.67 (m, 5 H, Ar); 8.10 (s, 1 H, Ar)	1630	2220	3240, 3350, 3465
b	3.87 (br.s, 3 H)	6.57 (br.s, 2 H)	7.03—7.08 (m, 2 H, Ar); 7.27—7.58 (m, 3 H, Ar); 7.75 (br.s, 1 H, Ar), 8.10 (d, 1 H, Ar, *J* = 8.6)	1638	2220	3260, 3360, 3480
c	3.88 (br.s, 3 H)	6.51 (br.s, 2 H)	6.96—7.39 (m, 2 H, Ar); 7.39—7.69 (m, 4 H, Ar); 8.10 (s, 1 H, Ar)	1637	2221	3242, 3360, 3460
d	3.88 (br.s, 3 H)	6.60 (br.s, 2 H)	7.13—7.41 (m, 5 H, Ar); 7.71 (s, 1 H, Ar); 8.03—8.13 (m, 1 H, Ar)	1635	2220	3250, 3360, 3460
e	3.74—3.98 (m, 3 H)	6.51 (br.s, 2 H)	6.68 (s, 1 H, Ar); 7.78—7.87 (m, 5 H, Ar); 8.12 (d, 1 H, Ar, *J* = 7.6)	1635	2222	3230, 3320, 3460
f	3.90 (m, 3 H)	6.47 (br.s, 2 H)	7.08 (d, 1 H, H(5´), *J* = 7.8); 7.19—7.31 (m, 4 H, Ar); 7.80 (s, 1 H, Ar); 8.10 (d, 1 H, Ar, *J* = 7.8)	1632	2220	3240, 3370, 3445
g	3.90 (br.s, 3 H)	6.52 (br.s, 2 H)	7.05 (d, 1 H, Ar, *J* = 8.9); 7.20 (s, 2 H, Ar); 7.65 (s, 1 H, Ar); 8.10 (t, 1 H, C(4´)H, *J* = 5.1); 8.82 (s, 1 H, C(6´)); 8.88 (s, 1 H, C(2´))	1625	2220	3220, 3340, 3400
h	3.90 (br.s, 3 H)	6.47 (br.s, 2 H)	7.10 (d, 1 H, H(4´), *J* = 5.2); 7.31—7.40 (m, 2 H, Ar); 7.85 (s, 1 H, Ar); 8.00—8.08 (m, 2 H, Ar)	1632	2220	3240, 3350, 3462
i	3.89 (br.s, 3 H)	6.48 (br.s, 2 H)	7.03—7.63 (m, 6 H, Ar); 8.09 (s, 1 H, Ar)	1623	2220	3240, 3360, 3460
j	3.90 (br.s, 3 H)	6.49 (br.s, 2 H)	7.00—7.10, 7.60—7.80 (both m, 3 H each, Ar); 8.09 (s, 1 H, Ar)	1635	2230	3240, 3360, 3440
k	3.88 (br.s, 3 H)	6.52 (br.s, 2 H)	7.01—7.20 (m, 3 H, Ar); 7.69 (d, 2 H, Ar, *J* = 8.96); 8.15—8.41 (m, 2 H, Ar); 8.82 (s, 1 H, H(6´)); 8.88 (s, 1 H, H(2´))	1630	2220	3240, 3360, 3460
l	3.89 (br.s, 3 H)	6.41 (br.s, 2 H)	7.05 (m, 1 H, Ar); 7.22 (s, 1 H, Ar); 7.30—7.55 (m, 3 H, Ar); 7.60—7.70 (m, 1 H, Ar); 8.10 (d, 1 H, H(6´), *J* = 7.8)	1633	2230	3240, 3370, 3460
m	3.88 (br.s, 3 H)	6.50 (br.s, 2 H)	7.03—7.18 (m, 3 H, Ar); 7.55 (s, 1 H, Ar); 7.82—8.10 (m, 3 H, Ar)	1640	2220	3240, 3360, 3462
n	3.90 (br.s, 3 H)	6.51 (br.s, 2 H)	6.95—7.20 (m, 3 H, Ar); 7.60—7.80 (m, 2 H, Ar); 8.10 (s, 1 H, Ar)	1624	2216	3264, 3376, 3464
o	3.86 (br.s, 3 H)	6.53 (br.s, 2 H)	6.92—7.22, 7.32—7.63 (both m, 2 H each, Ar); 7.89, 8.10 (both s, 1 H each, Ar)	1630	2230	3240, 3360, 3440
p	3.89 (br.s, 3 H)	6.46 (br.s, 2 H)	7.02—7.42 (m, 2 H, Ar); 7.61 (s, 1 H, Ar); 8.10 (t, 2 H, Ar, *J* = 5.0); 8.71, 8.85 (both s, 1 H each, Ar)	1632	2220	3180, 3320, 3410
q	3.89 (br.s, 3 H)	6.54 (br.s, 2 H)	7.07 (d, 2 H, Ar, *J* = 4.7); 7.33 (s, 2 H, Ar); 7.97—8.05 (m, 2 H, Ar)	1638	2220	3220, 3370, 3470
r	3.73 (br.s, 3 H)	6.47 (br.s, 2 H)	3.88 (br.s, 3 H, COOC$\underline{H}_3$); 6.64 (s, 1 H, Ar); 6.93 (br.s, 1 H, Ar); 7.38 (s, 1 H, Ar); 7.52—7.61, 8.00—8.10 (both m, 2 H each, Ar)	1632	2208	3384, 3712, 3752

Scheme 7



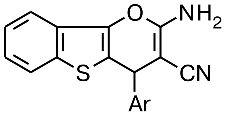
15: Ar = 4-ClC$_6$H$_4$ (**a**), 4-BrC$_6$H$_4$ (**b**)

arylmethylidenemalononitriles **2**, by the three-component condensation of benzo[*b*]thiophen-3(2*H*)-one (**12**), the corresponding aldehyde **10**, and malononitrile **6**. In fact, heating of compound **12** with malononitrile **6** (1 mol) in EtOH in the presence of Et$_3$N produces 2-amino-4-aryl-4*H*-[1]benzothieno[3,2-*b*]pyran-3-carbonitriles **13** (method *C*, Scheme 8). The relative yields of these compounds with various substituents are presented in Table 5. The structures of compounds **3** and **13** were

Table 5. Physicochemical characteristics of compounds **13a—f**

Compound **13**	Ar	Yield (%) (method)	M.p. /°C	Found/Calculated (%)				Molecular formula	MS, *m/z* ($[M]^+$)
				C	H	N	S		
a	Ph	28 (*A*)	218—220	69.51 71.03	4.31 3.97	9.45 9.20	10.52 10.54	$C_{18}H_{12}N_2OS$	304
b	4-ClC_6H_4	18 (*A*), 20 (*B*), 31 (*C*)	280—282	63.67 63.81	3.13 3.27	8.15 8.27	9.48 9.46	$C_{18}H_{11}ClN_2OS$	339
c	4-BrC_6H_4	21 (*A*), 38 (*B*), 48 (*C*)	275—277	56.02 56.41	2.57 2.89	7.55 7.31	8.39 8.37	$C_{18}H_{11}BrN_2OS$	383
d	2-FC_6H_4	36 (*C*)	219—221	67.81 67.07	3.89 3.44	8.30 8.69	9.93 9.95	$C_{18}H_{11}FN_2OS$	322
e	3-py	18 (*C*)	264—266	66.82 66.87	3.43 3.63	13.90 13.76	10.51 10.50	$C_{17}H_{11}N_3OS$	305
f	2-Thienyl	33 (*C*)	248—250	61.82 61.91	3.43 3.25	8.94 9.03	20.65 20.66	$C_{16}H_{10}N_2OS_2$	310

Table 6. Spectroscopic characteristics of compounds **13a—f**

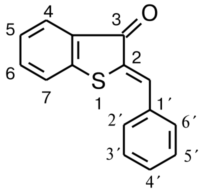


Compound **13**	^1H NMR, δ (*J*/Hz)			IR, ν/cm^{-1}		
	H(4) (s, 1 H)	2-NH_2 (br.s, 2 H)	Ar	δ(NH_2)	ν(CN)	ν(NH_2)
a	5.06	7.08	7.38—8.12 (m, 9 H)	1654	2226	3233, 3312, 3365
b	5.08	7.11	7.35 (t, 2 H, *J* = 8.14); 7.48—7.55 (m, 4 H); 7.86—8.00 (m, 2 H)	1654	2225	3216, 3245, 3430
c	5.07	7.08	7.25 (d, 1 H, *J* = 7.14); 7.44—7.62 (m, 5 H); 7.62—7.73 (m, 1 H); 7.88 (d, 1 H, *J* = 8.45)	1656	2224	3240, 3320, 3472
d	5.08	7.10	7.35—7.42 (m, 3 H); 7.54 (s, 1 H); 7.75 (t, 2 H, *J* = 10.55); 7.96—8.01 (m, 2 H)	1655	2224	3215, 3247, 3428
e	4.95	7.08	7.30 (br.s, 2 H); 7.46—7.73 (m, 4 H); 7.90—8.12 (m, 2 H)	1656	2227	3215, 3270, 3370
f	4.95	7.10	7.41 (s, 1 H); 7.54 (d, 1 H, *J* = 7.14); 7.75—7.96 (m, 3 H); 8.19—8.38 (m, 2 H)	1655	2225	3218, 3253, 3382

Table 7. Physicochemical characteristics of compounds **15a,b**

Compound **15**	R	Yield (%)	M.p. /°C	Found/Calculated (%)		Molecular formula	MS, *m/z* ($[M]^+$)
				C	H		
a	4-ClC_6H_4	46	165—167	65.91 66.05	3.48 3.33	$C_{15}H_9ClOS$	273
b	4-BrC_6H_4	57	180—182	56.85 56.80	2.84 2.86	$C_{15}H_9BrOS$	317

Table 8. Spectroscopic characteristics of compounds **15a,b**



Compound **15**	^{1}H NMR, δ (*J*/Hz)		IR, ν(CO)/cm^{-1}
	—CH= (s, 1 H)	Ar	
a	6.61	7.11 (d, 1 H, *J* = 7.35); 7.31—7.53 (m, 5 H); 7.83 (t, 2 H, H(2′), H(6′), *J* = 8.4)	1676
b	6.63	7.70 (d, 1 H, *J* = 7.75); 7.38—7.50 (m, 3 H); 7.85—7.98 (m, 2 H)	1682

confirmed by the data of physicochemical analyses (see Tables 3—6).

Scheme 8

$$\underset{}{\mathbf{12}} + \underset{\mathbf{10c,d,e,m}}{\text{ArCHO}} + \mathbf{6} \xrightarrow[\Delta]{Et_3N} \mathbf{13b,d,e,f}$$

13: Ar = 4-ClC$_6$H$_4$ (**b**), 2-FC$_6$H$_4$ (**d**), 3-py (**e**), 2-thienyl (**f**)

The IR spectra of compounds **3** are characterized by the absorption bands of deformation and stretching vibrations of the amino group at 1623—1650 and 3180—3460 cm^{-1}, respectively. The absorption bands of vibrations of the conjugated cyano groups in the enaminonitrile fragment of the aniline cycle appear at 2208—2230 cm^{-1}. The ^{1}H NMR spectroscopic data do not contradict the structure of annelated anilines **3**. For example, along with signals of the protons of the methoxy group (δ 3.74—3.98) and aryl substituent (δ 6.68—8.85), the ^{1}H NMR spectrum contains the characteristic moderately broadened signal from the protons of the amino group at δ 6.41—6.60.

The IR spectra of compounds **13** manifest absorption bands of deformation and stretching vibrations of the amino group at 1654—1655 and 3215—3472 cm^{-1}, respectively. The absorption bands of the conjugated cyano groups of the enaminonitrile fragment in the pyran cycle are detected in the 2224—2227 cm^{-1} interval. A similar pattern is observed in the IR spectra of benzannelated 2-amino-4*H*-pyrans.[7—9]

The ^{1}H NMR spectroscopic data agree with the structure of annelated pyrans **13**. For example, the ^{1}H NMR spectrum contains the characteristic signal of C(4)H as a singlet (δ 4.95—5.07) along with the signals from the protons of the benzothiophene and aryl fragments (δ 7.30—8.68). The signals of the protons of the amino group appear as a singlet at δ 7.08—7.10.

It is most probable that the differences in the reactivity of compounds **1** and **12** are related to the different electrophilicities of the C atom in position 3. It is most likely that in benzofuranone **1** the electrophilicity of the C atom in the carbonyl group is higher than that in benzothiophenone **12**. Therefore, compound **1** primarily enters into the Knoevenagel reaction and then undergoes transformation into dibenzofuran **3**.

Thus, the study of the reactions of 6-methoxybenzo[*b*]furan-3(2*H*)-one (**1**) and benzo[*b*]thiophen-3(2*H*)-one (**12**) with malononitrile and aldehydes allowed us to develop the regioselective methods for the synthesis of 2-amino-4-aryl-1,3-dicyano-7-methoxydibenzo[*b*,*d*]furans **3** and 2-amino-4-aryl-3-cyano-4*H*-benzothieno[3,2-*b*]pyrans **13**, respectively.

Experimental

Melting points of the synthesized compounds were determined on a Koffler stage. IR spectra of the compounds were recorded on a Specord IR-75 instrument in pellets with KBr. ^{1}H NMR spectra were detected on a Bruker M-300 instrument. The reaction course and purity of products were monitored by TLC on the Silufol UV-254 plates.

Compounds **1** [10] and **12** [11] were synthesized according to previously described procedures.

Synthesis of compounds 7a—c (general procedure). A solution of equimolar amounts of compound **1** (1.64 g, 0.01 mol) and aldehyde **10a—c** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et$_3$N (0.3 mL). The reaction mixture was stored for 24 h at 20 °C. A precipitate that formed was filtered off and washed with EtOH and hexane (see Tables 1 and 2).

Synthesis of compounds 3a—h (general procedure). ***A.*** A solution of equimolar amounts of compound **1** (1.64 g, 0.01 mol) and arylmethylidenemalononitrile **2a—h** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et$_3$N (0.3 mL). The reaction mixture was refluxed with stirring for 30 min and then stored for 24 h at 20 °C. A precipitate was filtered off and washed with EtOH and hexane (see Tables 3 and 4).

Synthesis of compounds 3b,d (general procedure). ***B.*** A solution of equimolar amounts of compound **7a,b** (0.01 mol) and malononitrile **6** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et$_3$N (0.3 mL). The reaction mixture was refluxed with stirring for 30 min and then stored for 24 h at 20 °C. A precipitate was filtered off and washed with EtOH and hexane (see Tables 3 and 4).

Synthesis of compounds 3b—d,g,i—r (general procedure). ***C.*** A solution of equimolar amounts of compound **1** (1.64 g, 0.01 mol), aldehyde **10a—n** (0.01 mol), and malononitrile **6** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et$_3$N (0.3 mL). The reaction mixture was refluxed with stirring for 30 min and then stored for 24 h at 20 °C. A precipitate was filtered off and washed with EtOH and hexane (see Tables 3 and 4).

Synthesis of compounds 13a—c (general procedure). ***A.*** A solution of equimolar amounts of compound **1** (1.50 g, 0.01 mol) and arylmethylidenemalononitrile **2a,b,e** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et_3N (0.3 mL). The reaction mixture was stored for 24 h at 20 °C. A precipitate was filtered off, washed with EtOH and hexane, and recrystallized from MeCN (see Tables 5 and 6).

Synthesis of compounds 13b,f (general procedure). ***B.*** A solution of equimolar amounts of compound **15a,b** (0.01 mol) and malononitrile **6** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et_3N (0.3 mL). The reaction mixture was stored for 24 h at 20 °C. A precipitate was filtered off, washed with EtOH and hexane, and recrystallized from MeCN (see Tables 5 and 6).

Synthesis of compounds 13b,d,e,f (general procedure). ***C.*** A solution of equimolar amounts of compound **1** (1.50 g, 0.01 mol), aldehyde **10c,f,d,m** (0.01 mol), and malononitrile **6** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et_3N (0.3 mL). The reaction mixture was stored for 24 h at 20 °C. A precipitate was filtered off, washed with EtOH and hexane, and recrystallized from MeCN (see Tables 5 and 6).

Synthesis of compounds 15a,b (general procedure). A solution of equimolar amounts of compound **12** (1.50 g, 0.01 mol) and aldehyde **10a,b** (0.01 mol) in EtOH (30 mL) was added at 40—60 °C by Et_3N (0.3 mL). The reaction mixture was stored for 24 h at 20 °C. A precipitate was filtered off and washed with EtOH and hexane (see Tables 7 and 8).

References

1. V. S. Velezheva, D. E. Gedz´, D. V. Gusev, A. S. Peregudov, B. V. Lekshin, and Z. S. Klemenkova, *Tez. dokl. 1-i Mezhdunar. konf. "Khimiya i biologicheskaya aktivnost´ azotistykh geterotsiklov i alkanov"* [*Abstrs. 1st Intern. Conf. "Chemistry and Biological Activity of Nitrogen-containing Geterocycles and Alkaloid*] (*Moscow, October 9—12, 2000*), Iridium Press, Moscow, 2001, **1**, 247 (in Russian).
2. V. S. Velezheva, K. V. Nevskii, and N. N. Suvorov, *Khim. Geterotsikl. Soedin.*, 1985, 230 [*Chem. Heterocycl. Compd.*, 1985, **21**, 235 (Engl. Transl.)].
3. O. Naumov and A. Shestopalov, *Abstrs. 7th Blue Danube Symp. on Heterocyclic Chemistry (Eger, Hungary, 1998)*, Eger, 1998, 124.
4. C. J. Adams and L. Main, *Tetrahedron*, 1991, **47**, 4979.
5. Yu. A. Sharanin, V. K. Promonenkov, and V. P. Litvinov, *Malononitril*, *Itogi nauki i tekhniki, Ser. Organicheskaya khimiya* [*Malononitrile, Advances in Science and Technology, Ser. Organic Chemistry*], VINITI, Moscow, 1991, **20**, Part 1, 239 pp. (in Russian).
6. M. Dewar and R. Doherti, *Teoriya vozmushchenii molekulyarnykh orbitalei v organicheskoi khimii* [*Perturbation Theory of Molecular Orbitals in Organic Chemistry*], Mir, Moscow, 1977, 273 pp. (Russ. Transl.).
7. Yu. A. Sharanin, V. K. Promonenkov, and L. G. Sharanina, *Zh. Org. Khim.*, 1982, **18**, 625 [*J. Org. Chem. USSR*, 1982, **18**, 544 (Engl. Transl.)].
8. Yu. A. Sharanin, L. N. Shcherbina, L. G. Sharanina, and V. V. Puzanova, *Zh. Org. Khim.*, 1983, **19**, 164 [*J. Org. Chem. USSR*, 1983, **19**, 150 (Engl. Transl.)].
9. M. S. Chauhan and I. W. J. Still, *Can. J. Chem.*, 1975, **53**, 2880.
10. A. Blom and J. Tambor, *Ber.*, 1905, **38**, 3590.
11. C. Hansch and H. G. Lindwell, *J. Org. Chem.*, 1945, **10**, 383.

Received October 2, 2002;
in revised form December 19, 2002