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11H-ISOINDOLO[2,1-*a*]BENZIMIDAZOLES (REVIEW)

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Data on methods for the synthesis of isoindolo[2,1-a]benzimidazole and its derivatives and their chemical characteristics are reviewed. Data from quantum-chemical calculations of certain structures are presented. Possible practical applications of the compounds are indicated.

Keywords: 5H-isoindolo[2,1-*a*]benzimidazoles, 11H-isoindolo[2,1-*a*]benzimidazoles, 11H-isoindolo [2,1-*a*]benzimidazol-11-ones, 11H-isoindolo[2,1-*a*]benzimidazole 11-imines, pyrrones, poly(isoindolo [2,1-*a*]benzimidazolones), polymers, biological activity, reactivity, synthesis.

Investigation of the chemical characteristics of isoindole derivatives is an important direction in the chemistry of heterocyclic compounds [1-3]. Among published papers on the chemistry of condensed isoindoles it is possible to mention reviews on triazolo- and tetrazoloisoindoles [4] and also on the pyrido- and pyrimidoisoindoles [5]. In the present review we examine data published up to May 2006 on the synthesis, chemical transformations, and important practical characteristics of the derivatives of isoindolo[2,1-*a*]-benzimidazole.

The heterocyclic system of isoindolo[2,1-*a*]benzimidazole is of interest mainly on account of the practical importance of its derivatives in industry as dyes and as pigments for fibers and plastics. Polymers with an isoindolobenzimidazole fragment are also very widely used.

Methods for the synthesis of derivatives of 11H-isoindolo[2,1-*a*]benzimidazole (section 1) are examined, and the existing theoretical and spectroscopic data for these compounds (section 2) are discussed. Data on the chemical characteristics are presented in section (3). Attention is then paid to the practical importance of both low-molecular and polymeric derivatives of isoindolo[2,1-*a*]benzimidazole (section 4), and data on the biological activity of the compounds are also examined (section 5).

1. METHODS OF SYNTHESIS

1.1. Methods of Construction of the 11H-Isoindolo[2,1-*a*]benzimidazole System

1.1.1. Reaction of *o*-Arylenediamines with Bifunctional Compounds – *o*-Disubstituted Arenes. The most widely used methods for the synthesis of the various isoindolo[2,1-*a*]benzimidazoles are based on the reaction of the two NH_2 groups of *o*-arylenediamines with the two substituents of *o*-disubstituted arenes.

Thus, in 1906 Thiele and Falk [6] first produced 11H-isoindolo[2,1-*a*]benzimidazole (**3a**) from *o*-phenylenediamine (**1a**) and phthalic anhydride (**2a**) (yield not indicated). Its structure was confirmed by oxidation to 11H-isoindolo[2,1-*a*]benzimidazole-11-one (**4a**). The results of this work were subsequently re-examined, and the product from the condensation of compounds **1a** and **2a** was assigned the structure of

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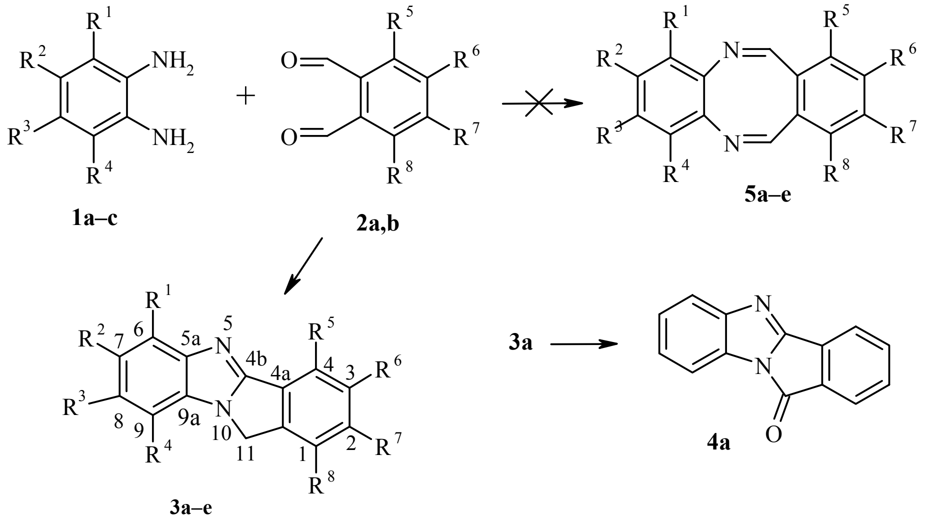
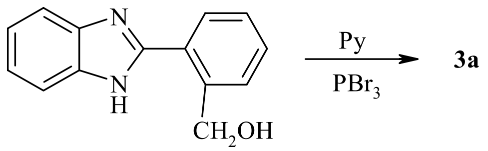
the diazocine **5a** [7]. Similarly, the structure of bisannelated diazocines **5b-c** was proposed for the products obtained from 2,3-naphthalenedialdehyde **2b** and the diamine **1a** [8], 2,3- and 1,2-diaminonaphthalenes (**1b** and **1c** respectively) [9], and also from the dialdehyde **2a** and 2,3-diaminonaphthalene **1b** [9].



1 a $R^1 = R^2 = R^3 = R^4 = H$, **b** $R^1 = R^4 = H$, $R^2+R^3 = Z$, **c** $R^1+R^2 = Z$, $R^3 = R^4 = H$;
2 a $R^5 = R^6 = R^7 = R^8 = H$, **b** $R^5 = R^8 = H$; $R^6+R^7 = Z$;
3, **5 a** $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = H$, **b** $R^1 = R^2 = R^3 = R^4 = R^5 = R^8 = H$, $R^6+R^7 = Z$,
c $R^1 = R^4 = R^5 = R^8 = H$, $R^2+R^3 = R^6+R^7 = Z$, **d** $R^1+R^2 = R^6+R^7 = Z$, $R^3 = R^4 = R^5 = R^8 = H$;
e $R^1 = R^4 = R^5 = R^6 = R^7 = R^8 = H$, $R^2+R^3 = Z$; Z = CH=CH–CH=CH

However, the results of subsequent investigations showed that all the above-mentioned products have structures **3a-e** and not **5a-e**. Thus, the structure of compound **3a** was confirmed by the results from the action of sodium 1,2-naphthoquinonesulfonate on it in DMFA (the solution was dark-green, which is a qualitative reaction for the presence of a benzylamine or indole fragment in the molecule) [10], by an alternative synthesis from *o*-(imidazol-2-yl)benzyl alcohol (**6**) (yield 18.4%) [11, 12], and by the data from the ^{1}H NMR spectrum and by comparison of the UV spectrum with the UV spectra of 1-benzyl-2-phenylbenzimidazole and the azomethine obtained from benzaldehydes and aniline [13].



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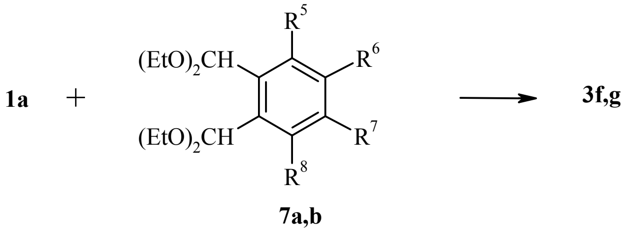
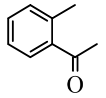
The structure of compounds **3b-e** was confirmed by the data from the ^{1}H NMR spectra [13, 14].

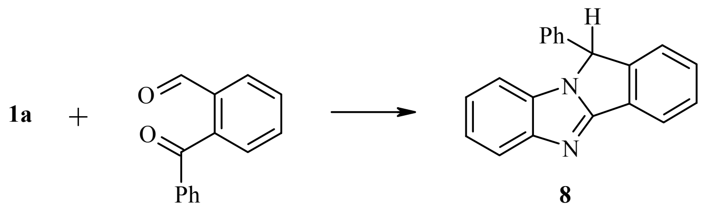
A fluorimetric method for the determination of ortho-phenylenediamine in the presence of the *meta* and *para* isomers was proposed on the basis of the reaction of the diamine **1a** with *o*-phthalic anhydride [15].

Instead of dialdehydes of type **2** it is possible to use the structurally similar diacetals for the construction of the isoindolo[2,1-*a*]benzimidazole system; the products **3f**, **g** were obtained (yields 83 and 8% respectively) from the diamine **1a** and the diacetals **7a**, **b** [16].

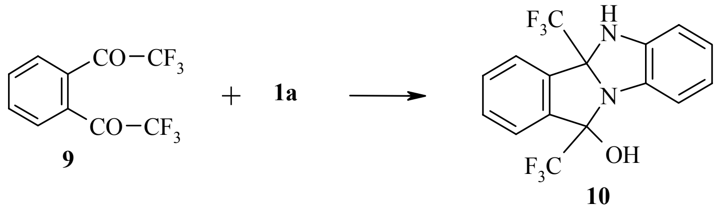


3f,g R^1–R^4 = H; **3f**, **7a** R^5–R^8 = Ph; **3g**, **7b** R^5 = R^8 = Ph, R^6+R^7 = 

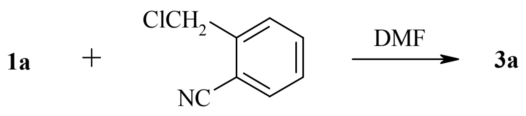
By substituting one of the CHO groups in the dialdehyde by a COR group it is possible to construct the isoindolobenzimidazole system with the substituent R at position 11. Thus, the 11-phenyl derivative **8** was synthesized from the diamine **1a** and *o*-benzoylbenzaldehyde [17].



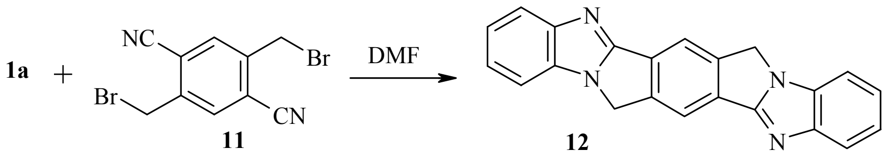
The product **10** was obtained with a yield of 86% by the condensation of the diamine **1a** with the *o*-arylene diketone **9** [18].



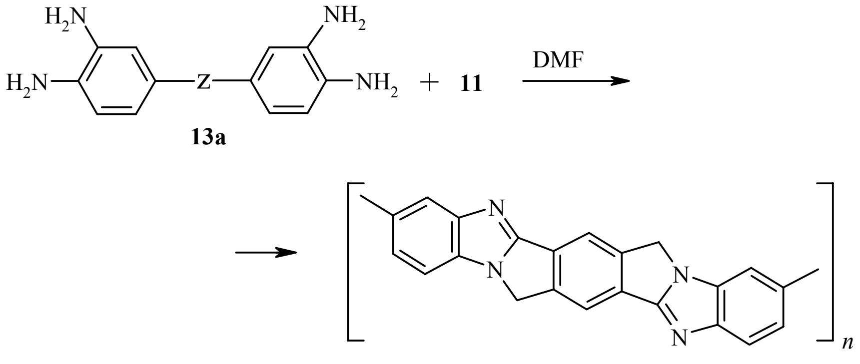
In addition to the above-mentioned dialdehydes **2** and diacetals **7** *o*-(chloromethyl)benzonitrile was also used successfully to construct system of type **3**. Babichev and co-workers proposed a method for the production of the isoindolobenzimidazole **3a** with a yield of 58% by condensation of the nitrile with the diamine **1a** [19].



Two molecules of the diamine **1a** react with compound **11**, which contains four functional groups, leading to the formation of the product **12** [20].

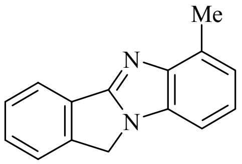


If the tetraamine **13a** is used instead of the diamine **1a**, the corresponding polymer is formed as a result of reaction with compound **11** [20]. Such polymers have probably not found practical application; there are no published data apart from the above-mentioned paper.

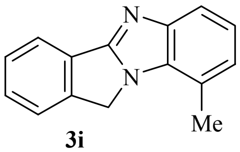


13a Z = bond

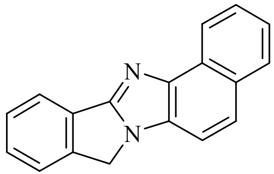
The reaction of *o*-(chloromethyl)benzonitrile with the unsymmetrical diamines 3-methyl-*o*-phenylenediamine and 1,2-diaminonaphthalene **1c** in both cases gave two isomeric products **3h**,**i** and **3j**,**k** respectively, which were separated by recrystallization [21].



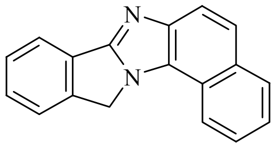
3h



3i

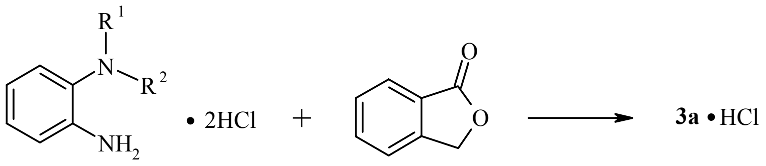


3j



3k

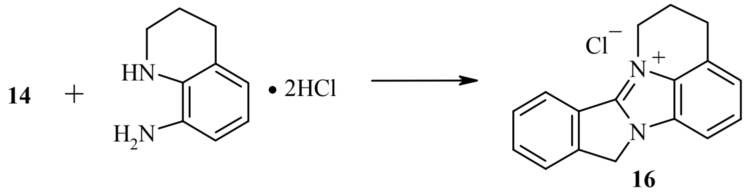
1.1.2. Reaction of *o*-Arylenediamines with Phthalide, Dithiophthalide, and Indolenines. Methods based on the reaction of *o*-arylenediamines **1** or their hydrochlorides with phthalides, dithiophthalides, and indolenines, acting as bifunctional compounds, are similar to the examples of the synthesis of isoindolo[2,1-*a*]benzimidazoles examined in section 1.1.1. For example, one of the methods for the production of isoindolobenzimidazole hydrochloride **3a**·HCl involves fusion of the phthalide **14** with the hydrochloride of the diamine **1a** or its N-ethyl- and N,N-diethyl-substituted derivatives **15a**,**b** at 200°C. The yields of the hydrochloride amount to 40, 40, and 15% respectively [22].



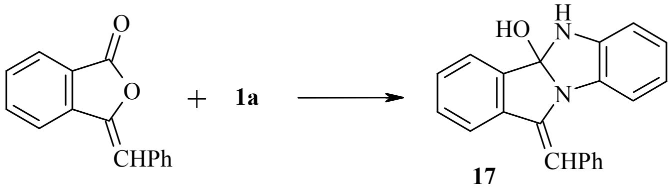
1a, 15a,b **14**

1a R^1 = R^2 = H; **15 a** R^1 = H, R^2 = Et; **b** R^1 = R^2 = Et

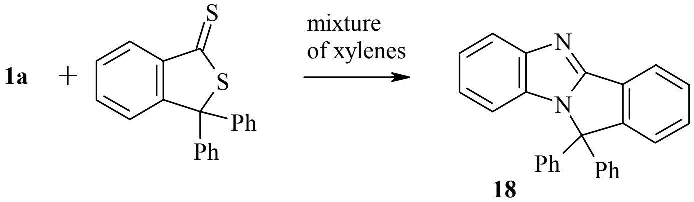
8-Aminotetrahydroquinoline can be used as diamine hydrochloride, and in this case the salt **16** is formed under similar conditions [23].



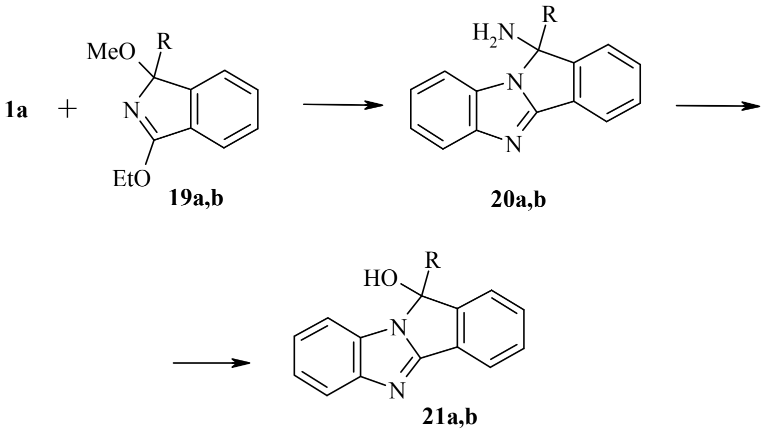
The alcohol **17** was synthesized similarly from the diamine **1a** and 3-benzylidenephthalide [24].



3,3-Diphenyldithiophthalide reacts similarly to phthalide with the diamine **1a**, giving an 84% yield of compound **18** [20]:

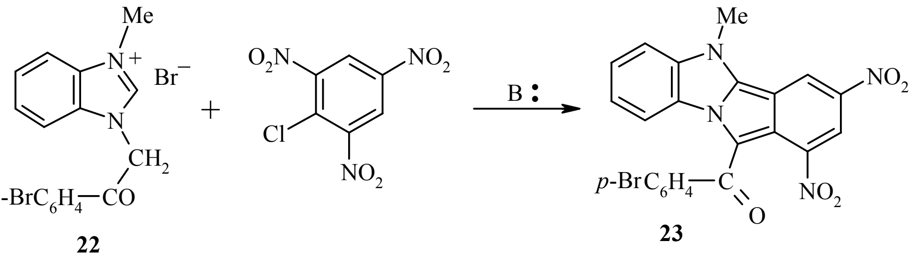


In [9] a method was proposed for the production of 11,11-disubstituted isoindolobenzimidazoles by condensation of the amine **1a** with indolenines **19a**, **b**. During hydrolysis of the products **20a**,**b** the corresponding alcohols **21a**,**b** are formed.

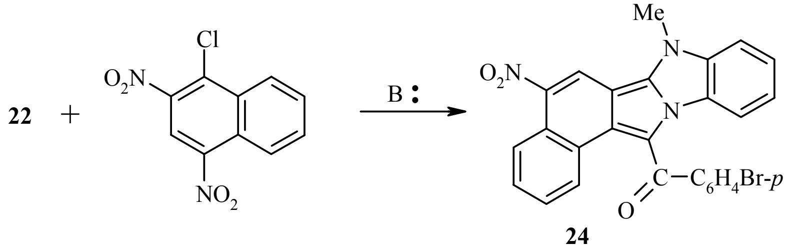


19–21 a R = Ph, **b** R = C_6H_4Cl-*p*

1.1.3. Synthesis from Polynitrohaloarenes (Kröhnke's Synthesis). According to data from Kröhnke, the reaction of substituted benzimidazolium methobromide **22** and picryl chloride in the presence of a base leads to the polysubstituted isoindolobenzimidazole **23** (yield 89%). Compound **24** was obtained similarly from the salt **22** and 2,4-dinitro-1-chloronaphthalene (yield 16%) [25].



22 **23**



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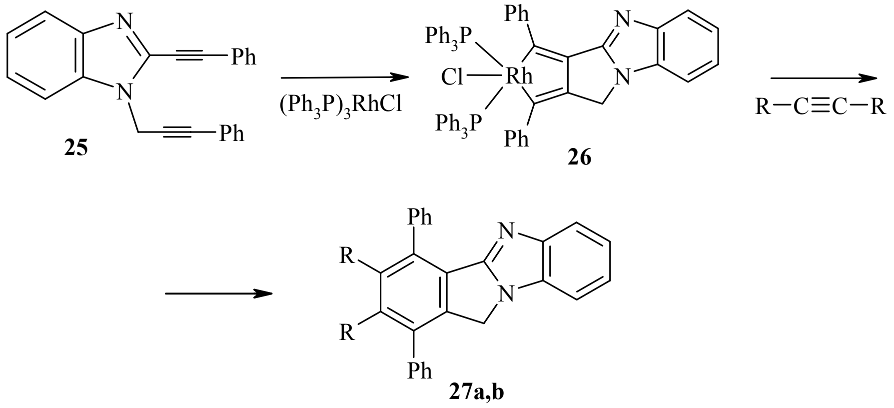
1.1.4. Synthesis using the Cyclopentadiene Complexes of Rhodium. An interesting method for the production of substituted isoindolo[2,1]benzimidazoles was proposed in [26]. With tris(triphenylphosphine)rhodium chloride the disubstituted benzimidazole **25** forms the product **26**. Treatment of the latter with diethyl acetylenedicarboxylate in xylene leads to the diester **27a** (yield 54%), while treatment with diphenylacetylene leads to the tetraphenyl-substituted compound **27b** (yield 85%) [26].

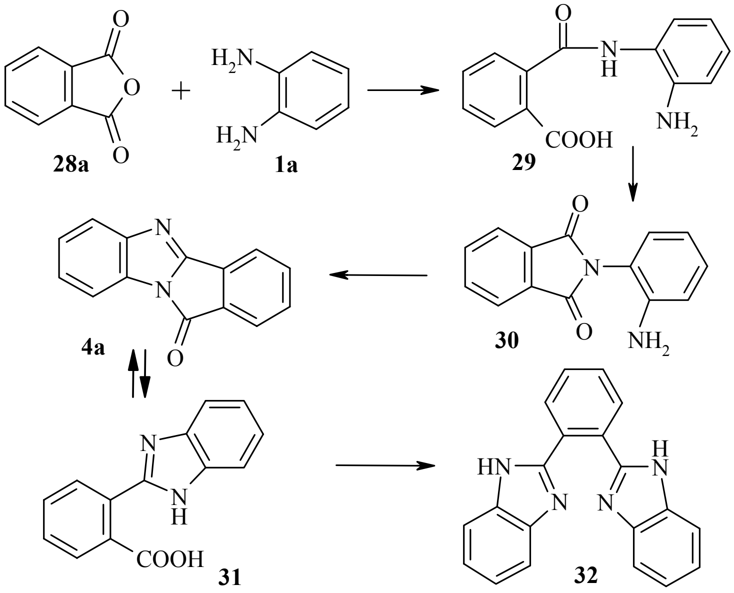


25 **26** **27a,b**

27 a R = COOEt, **b** R = Ph

1.2. Methods for the Production of 11H-Isoindolo[2,1-*a*]benzimidazol-11-ones and the 11-Imines

1.2.1. Reaction of *o*-Arylenediamines with Derivatives of Phthalic Acid. The most widely used method for the production of 11H-isoindolo[2,1-*a*]benzimidazol-11-one **4a** is based on the condensation of *o*-phenylenediamine **1a** with phthalic anhydride **28a** [7, 27]. Various products can be formed in this reaction (see the scheme below), depending on the conditions [28, 29]. At moderate temperature in methanol small amounts of the polyamide of phthalic acid **29** and substituted phthalimide **30** are formed [30]. With boiling only a mixture (1:1) of compound **30** and benzimidazolyl-substituted benzoic acid **31** is obtained. The composition of the mixture does not change with further heating [28]. In water and acetic acid when the boiling point of the reaction mass is reached the initially formed phthalimide **30** is mainly transformed into the substituted benzoic acid **31** and also (in small amounts) into the required isoindolobenzimidazolone **4a** and bis(2-benzimidazolyl)benzene **32** [28, 30]. Products with the same composition are obtained in pyridine, while in nitrobenzene the reaction is accelerated and the content of compound **4a** is increased [28].

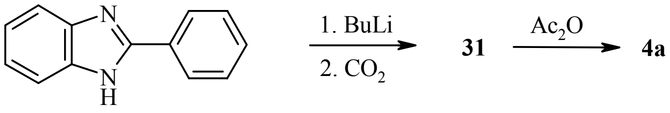


According to the data from the IR and ^{1}H NMR spectra [31], from compound **28a** in dimethylacetamide at 120 and then at 140 and 200°C the amide **29** is formed at the first stage, and the phthalimide **30** and isoindolobenzimidazolone **4a** are formed later.

During fusion of the anhydride **28a** and the diamine **1a** depending on the conditions compound **30**, **32**, or **4a** (according to the ^{1}H NMR data) is mostly formed. Thus, as a result of treatment of the reagents under vacuum the product **30** (32%) is formed at 115°C, **32** (49%) at 250°C, and **4a** (44%) at 140°C [32].

It is commonly held [29, 31, 32] that the transformation **30** → **4a** can occur at 195-200°C, while the transformation **31** → **4a** can only be realized at 240-270°C. Arient's conclusion that compound **31** is formed as a result of the hydrolysis of the isoindolobenzimidazolone **4a** [28, 30] does not agree with the data in [29, 32]. Either fusion of compounds (**29**) or (**30**) at 250-290°C or boiling in acetic anhydride is recommended for the synthesis of **4a** [28].

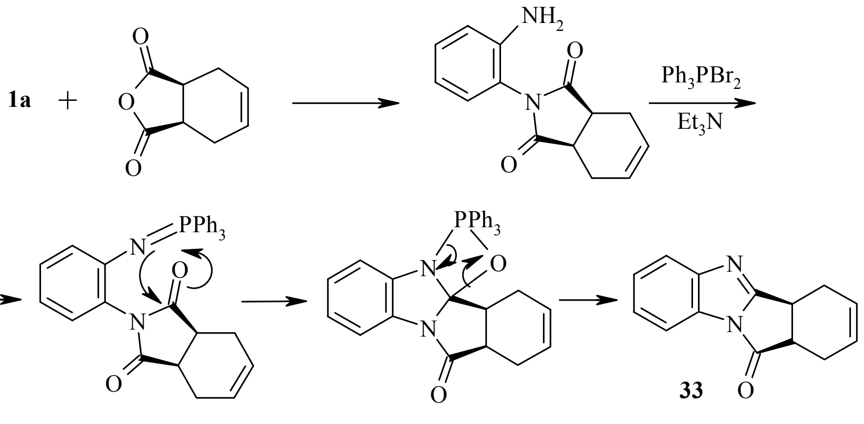
The acid **31** can also be obtained by a different method and brought into reactions leading to the desired isoindolo benzimidazolone **4a** starting, for example, from 2-phenylbenzimidazole [33]:



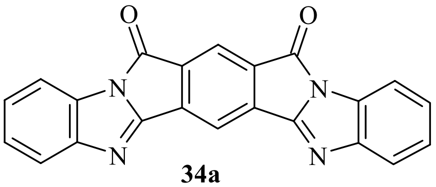
The complications in the production of compound **4a**, like the ease of its hydrolysis, are due to the fact that closure of the second five-membered ring in compounds **30** and **31** requires considerable deformation of their molecules, which can only be achieved under very harsh conditions.

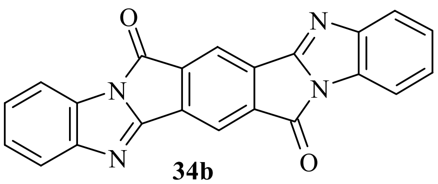
The reaction of phthalic anhydride with 2-nitroaniline under conditions of reduction of the latter (Fe + AcOH) also leads to the product **4a** with a yield of 90% [34].

A method was proposed for the synthesis of the partially hydrogenated isoindolobenzimidazolone **33** by the Wittig aza reaction (yield 48%) [35]:



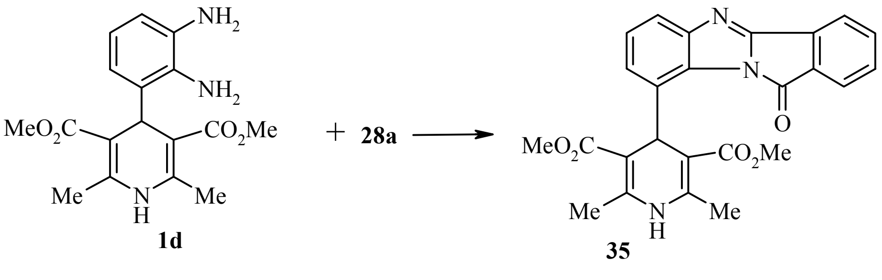
Compounds **34a**,**b** containing two fragments of isoindolobenzimidazolone and having a common benzene ring were also obtained from the diamine **1a** and pyromellitic dianhydride [36].


34a

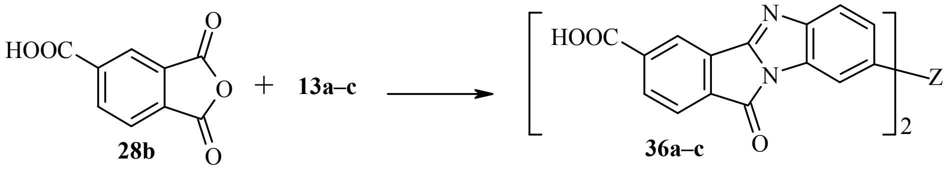

34b

The condensation of 3,3',4-tricarboxybiphenyl with the diamine **1a** in acetic acid led to 2-(3'-carboxyphenyl)isoindolo[2,1-*a*]benzimidazol-11-one, which provides evidence for the structure of the original tricarboxylic acid [37].

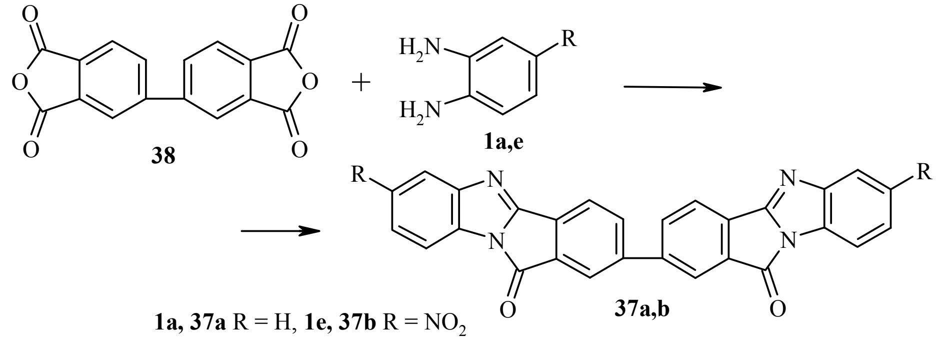
The corresponding isoindolobenzimidazolone **35** with a substituent at position 9 was obtained similarly (yield 55%) from phthalic anhydride **28a** and substituted phenylenediamine **1d** [38].



Compounds **36a-c** with two isoindolo[2,1-*a*]benzimidazole residues separated by a single bond, an oxygen atom, or a CH_2 group were synthesized by the condensation of the anhydride **28b** with the tetraamines **13a-c** [39, 40]. Similar products of type **37** were obtained from the dianhydride **38** and the diamines **1a**,**e** [41, 42]. The use of various aromatic tetraamines of the 1,2,4,5-tetraaminobenzene type in reactions with anhydrides is also known [43].

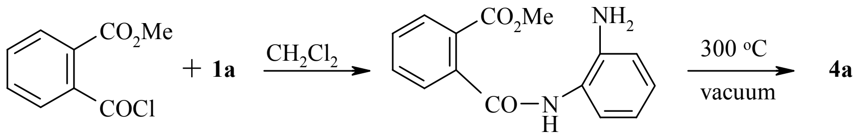


13, **36 a** Z = bond, **b** Z = O, **c** Z = CH$_2$

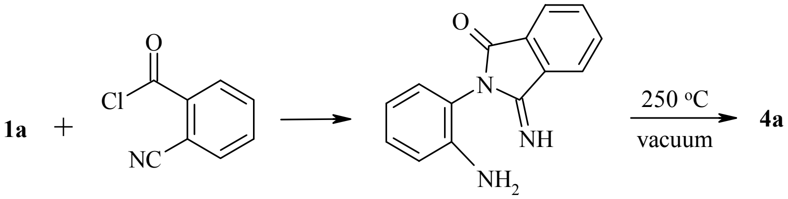


1a, 37a R = H, **1e, 37b** R = NO$_2$

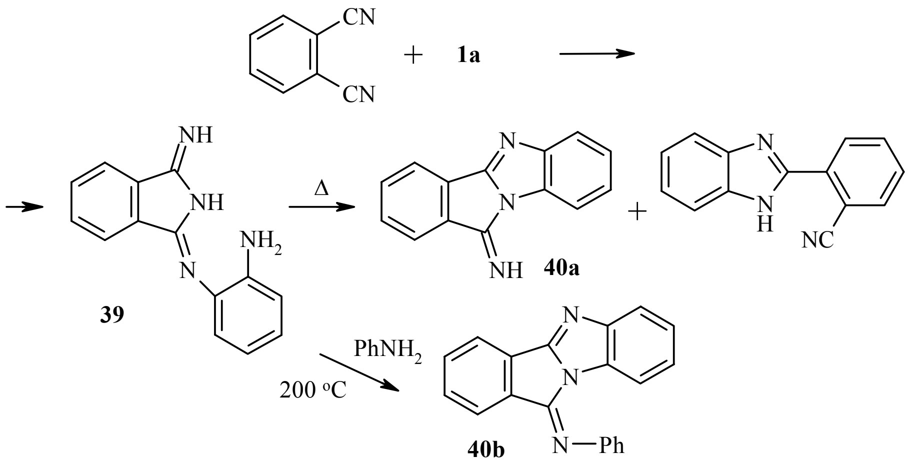
Other derivatives of phthalic acid, such as the chloride of its half-ester, can be used instead of the anhydrides for the production of isoindolo[2,1-*a*]benzimidazole-11-ones [36].



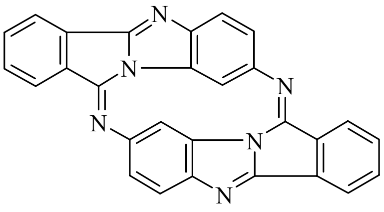
Treatment of the diamine **1a** with *o*-cyanobenzoyl chloride at 250°C under vacuum led to compound **4a** with a yield of 75% [44].



Compound **39** was synthesized with a yield of 85% by the condensation of phthalodinitrile with the diamine **1a** in the presence of sodium methoxide, and its thermolysis in an inert atmosphere gave 11-imino-11H-isoindolo[2,1-*a*]benzimidazole **40a** and 2-(2'-cyanophenyl)benzimidazole [45]. Treatment of compound **39** and aniline at 200°C in N-methylpyrrolidone led to the substituted imine **40b** (yield 75%).



Compound **41** was obtained with a yield of 90% from 1,2,4-triaminobenzene and phthalodinitrile. Its structure was confirmed by elemental analysis and by the IR spectrum [45]. The spectrum did not contain bands for the NH and NH_2 groups, but there were bands at 1660 and 1620 cm^{-1}, characteristic of the C=N fragment.



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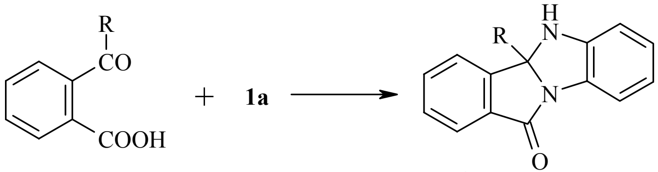
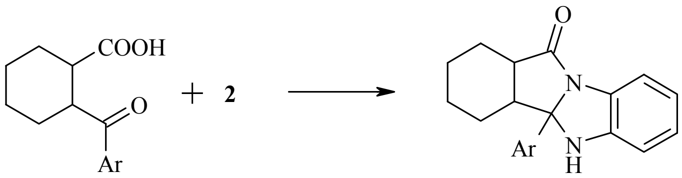
1.2.2. Reactions of *o*-Arylene diamines with *o*-Aroyl- and *o*-Acetylbenzoic Acids. The condensation of *o*-acylbenzoic acids [45-51] with the diamine **1a**, leading to substituted isoindolobenzimidazoles **42**, was studied [48].



42

R = H, Me, C_6H_4X, where X = *p*(*m*)-Cl, Br, F, CF_3, Me, Et, OMe, OEt

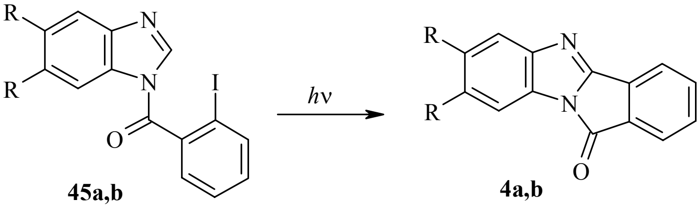
In the case of *o*-aroylcyclohexanecarboxylic acids the corresponding 4b-aryl-substituted 1,2,3,4-tetrahydroisoindolobenzimidazolones **44a**,**b** are formed with yields of ~50% [52-54].



43a,b **44a,b**

43, 44 a Ar = Ph, **b** Ar = C_6H_4Me-*p*

1.2.3. Other Reactions. Photolysis of 1-*ortho*-iodobenzoylbenzimidazoles **45a**,**b** was proposed for the synthesis of isoindolobenzimidazolones **4a**,**b** (product yields 34% of **4a**, 39% of **4b**) [55].

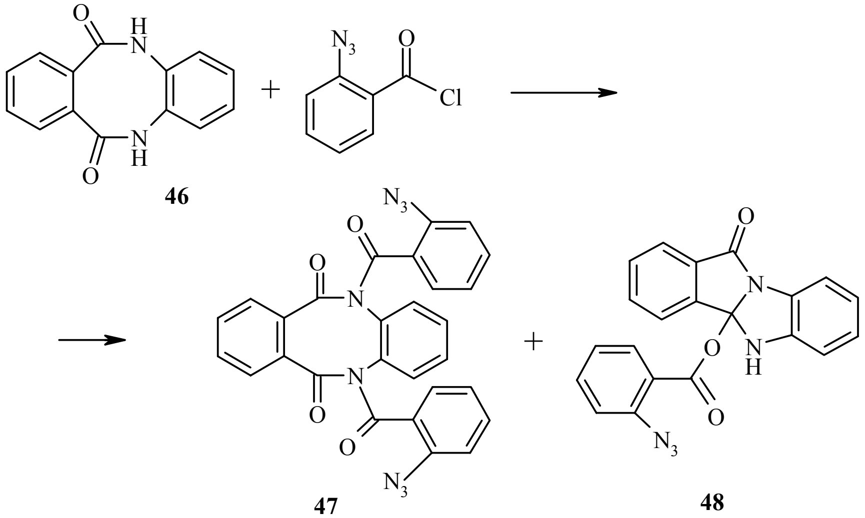


45a,b **4a,b**

4, 45 a R = H, **b** R = Me

Apart from photolysis it is possible to realize the cyclization of such compounds in the presence of $Pd(OAc)_2$–$2PPh_3$ as catalyst [56].

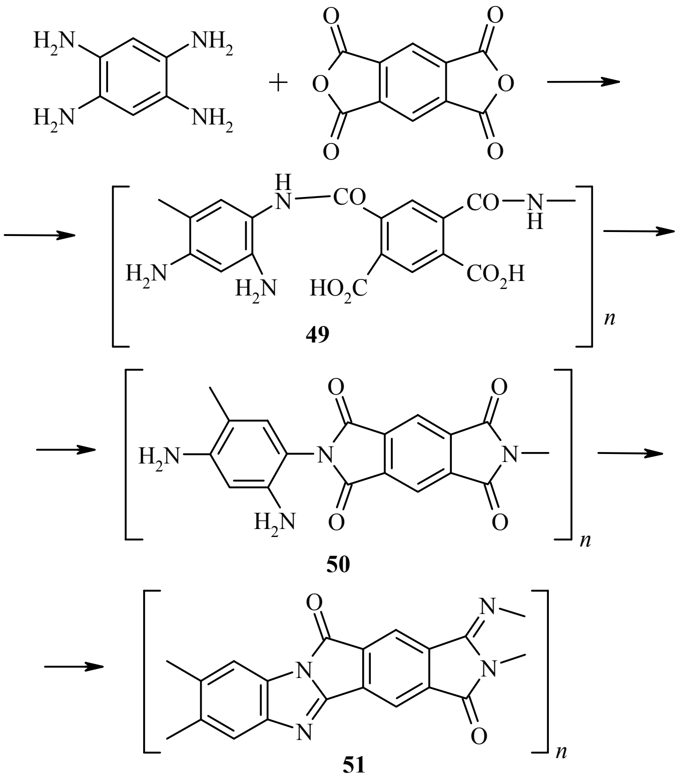
During the bis-2-azidobenzoylation of the diazocine **46** it was found that the substituted isoindolobenzimidazolone **48** was formed in addition to the desired product **47** [57].



46 **47** **48**

1.2.4. Polymeric Compounds with a Structural Isoindolo[2,1-*a*]benzimidazolone Ring. Possible variants of the reaction of *o*-phenylenediamine with phthalide anhydride were examined in section 1.2.1. Similar transformations occur during the reactions of aromatic dianhydrides with aromatic tetraamines, leading to polymers – poly(isoindolo[1,2-*a*]benzimidazolones), otherwise known as poly(aroylenebenzimidazoles) or simply as pyrones.

Pyrrones were first synthesized in 1965-1966 [31, 32, 58]. At the present time several reviews have been devoted to them [29, 31, 59], and we will not therefore discuss them in detail.



49

50

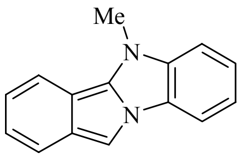
51

The dianhydrides of various 1,2,4,5-tetracarboxylic acids and tetraamines have been used for the production of pyrrones. The polyaminoamido acid **49**, polyaminoimide **50**, and finally the pyrrone **51** are formed successively during the reaction [59, 60]. (We will illustrate this for the case of the condensation of 1,2,4,5-tetraaminobenzene with pyromellitic anhydride.) The reaction rate decreases with increase in the rigidity of the chains, on account of which the degree of cyclization during the production of the pyrrones, determined by spectroscopy [61], amounts to 60-80% [60]. The thermodynamics of the synthesis of pyrrones were studied [62, 63].

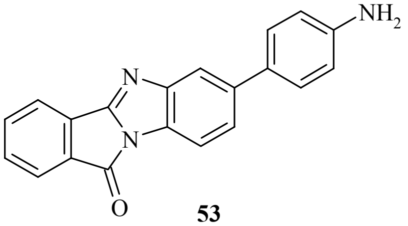
2. THEORETICAL AND PHYSICAL ASPECTS

2.1. Quantum-mechanical Calculations

On the basis of analysis of the localized molecular orbitals of 5-methyl-5H-isoindolo[2,1-*a*]-benzimidazole **52a** it was shown that its electronic structure can be represented in the form of three weakly interacting parts: The isoindole fragment, the electron pair of the nitrogen attached to the methyl group, and the benzene ring [64]. Thus, this compound can be considered to a first approximation an analog of 1,2-disubstituted isoindoles (10π-electron systems).



52a



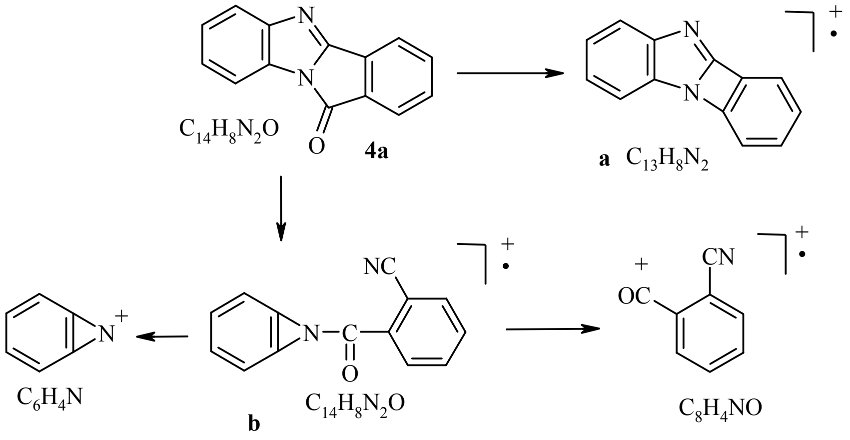
53

The results from calculation of the charges at the nitrogen atom of the NH$_2$ group in the phenyl substituent (q_N = 0.18) for compound **53** by the PPP method [65] demonstrate the electron-accepting characteristics of the 11H-isoindolo[2,1-*a*]benzimidazole-11-one fragment in relation to this group.

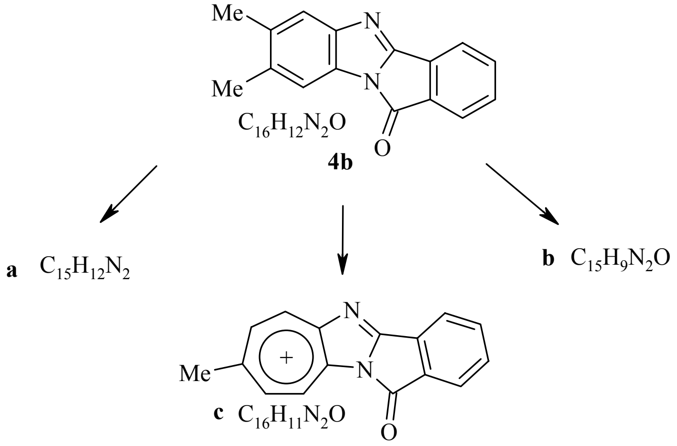
2.2. Mass Spectra

The results from analysis of the mass spectrum of compound **4a** [55, 66] indicate that fragmentation begins with loss of the CO group, leading to the ion **a**, or that ion **b** is formed as a result of ionization and dissociates further according to the scheme.

Scheme



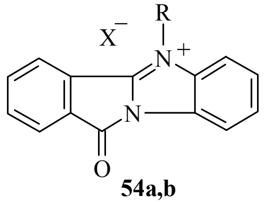
In the case of the 7,8-dimethyl-substituted compound **4b**, apart from elimination of the CO group leading to ion **a**, initial ejection of CH_3 or $H^{\cdot}$ with the formation of the respective ions **b** or **c** is also possible [66].



2.3. Data from the IR and UV Spectra and ^{1}H NMR Spectra

In the IR spectra of the isoindolo[2,1-*a*]benzimidazole-11-ones the frequencies of the stretching vibrations of the carbonyl group are at 1730-1765 cm^{-1} [29, 31, 67].

For the UV spectra of 11H-isoindolo[2,1-*a*]benzimidazole-11-one **4a** and the salts **54a**,**b** the λ_{max} (log ε) values are 338 (0.6), 278 (1.14), and 278 nm (1.11) respectively [68-70].



54a,b

54 a R = H, X = HSO_4, **b** R = Me, X = $MeSO_4$

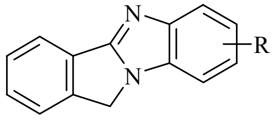
In the spectra of the compounds having an isoindole *ortho*-quinonoid structure there is a long-wave absorption band for compound **52a**, for example, at λ_{max} 414 nm (log ε 3.22) [64].

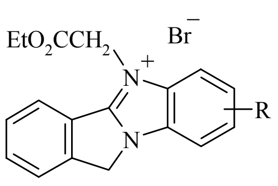
In the ^{1}H NMR spectrum of compound **3a** the signal for the protons of the CH_2 group is at 4.9 ppm, while the signals for the aromatic protons are in the region of 7.7-8.2 ppm [21].

In the ^{1}H NMR spectrum of compound **52a** the singlet of the protons of the CH_3 group is observed at 3.92 ppm, while the multiplet of the aromatic protons is at 6.42-7.64 ppm [23].

The structure of compounds **3h**-**k** was established with lanthanide shift reagents. It was found that the singlets of the CH_2 protons of compounds **3h** and **3j** are observed in the upfield region (4.95 and 4.81 ppm) compared with the analogous signals of the isomeric compounds **3i** and **3k** (5.19 and 5.15 ppm) respectively [21].

To obtain evidence for the structure of the product from the condensation of methoxy-substituted *o*-phenylenediamine with phthalic aldehyde compounds **3a**, **l** were quaternized with ethyl bromoacetate. On the basis of the differences in the chemical shifts in the ^{1}H NMR spectra of the methylammonium groups in the salts (**55a**, **b**) it was concluded that the OMe group in compounds **31** and **55b** is at position 7 [71].


3a,l

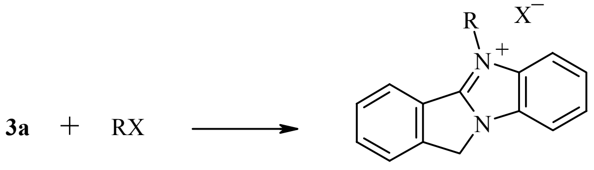

55a,b

3a, **55a** R = H, **3l**, **55b** R = OMe

3. CHEMICAL PROPERTIES

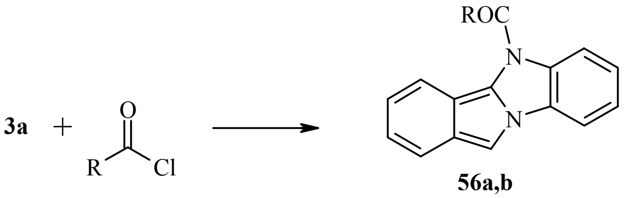
3.1. 11H-Isoindolo[2,1-*a*]benzimidazoles and 11H-Isoindolo[2,1-*a*]benzimidazolium Salts

3.1.1. Basic Characteristics. 11H-Isoindolo[2,1-*a*]benzimidazole **3a** is converted by the action of alkylating agents into the quaternary salts **55c-e**, which are soluble in water [22].


55c–e

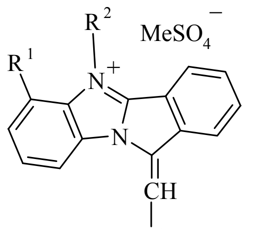
55 c, **d** R = Me, **c** X = MeSO$_4$, **d** X = I, **e** R = Et, X = I

When heated with acetic anhydride compound **3a** is readily acetylated with the formation of the 5-acetyl derivative **56a**, which is hydrolyzed by alkali to the initial base **3a**. The latter is converted by the action of BzCl into the 5-benzoyl derivative **56b** [72].

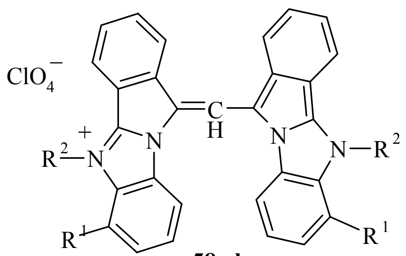

56a,b

56 a R = Me, **b** R = Ph

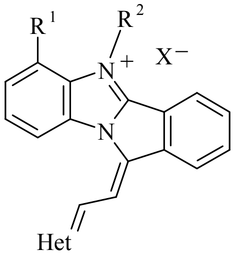
3.1.2. Condensation Reactions of 11H-Isoindolo[2,1-*a*]benzimidazolium Salts at the Methylene Group of the NCH$_2$ Fragment. 11H-Isoindolo[2,1-*a*]benzimidazolium salts of type **55** enter readily into condensation with aldehydes at the active methylene group at position 11 [22, 73]. This was used for the production of a series of cyanine dyes [22, 74] – the styrils **57a** and **57b** [yield 73%, λ_{max} 492 nm (log ε 4.67) and 22%, λ_{max} 497 nm (log ε 4.83) respectively], symmetrical monomethinecyanines **58a** and **58b** [yield 19.8%, λ_{max} 635 nm (log ε 5.15) and yield 18.5% respectively], and unsymmetrical dimethinecyanines **59a-l**.



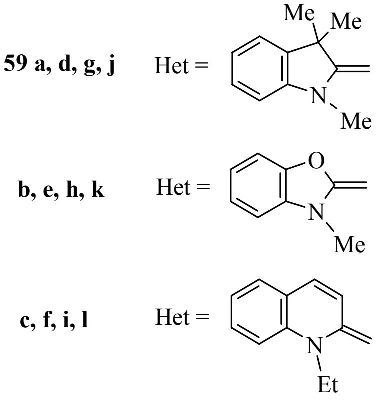
57a,b



58a,b

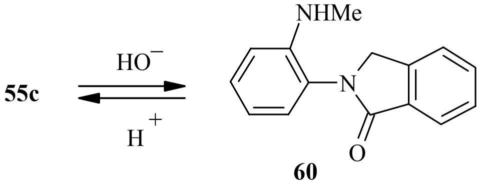


59a–l



57 a $R^1 = R^2 = H$, **b** $R^1 = H$, $R^2 = Me$; **58 a** $R^1 = H$, $R^2 = Et$, **b** R^1+$R^2 = (CH_2)_3$;
59 a–c $R^1 = R^2 = H$, **d–f** $R^1 = H$, $R^2 = Et$, **g–l** R^1+$R^2 = (CH_2)_3$; **a–i** $X = ClO_4$, **j–l** $X = I$

3.1.3. Opening the Imidazole Ring in 11H-Isoindolo[2,1-*a*]benzimidazolium Salts. The imidazole ring of the 11H-isoindolo[2,1-*a*]benzimidazolium salt **55c** is opened by the action of alkali with the formation of compound **60** [22, 72]. In [72] it was noticed that a yellow crystalline substance, which may be 5-methylisoindolo[2,1-*a*]benzimidazole, is formed initially.

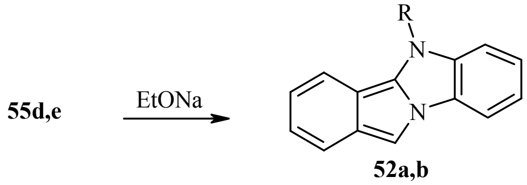


60

3.1.4. The Formation of Compounds with an *ortho*-Quinonoid System from 11H-Isoindolo[2,1-*a*]-benzimidazolium Salts. Treatment of the salts **55d**, **e** and **16** gave the corresponding salts with a 10π-electron aromatic system **52a**, **b** and **61** [23]. The aromatic characteristics of compound **52a** were first discussed in [75].

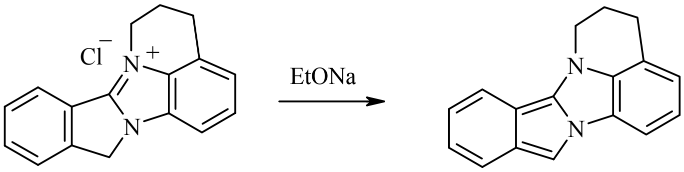
The bases **52** and **61**, which are bright-yellow crystalline substances, form salts with acids. During the action of water on them the imidazole ring is broken, and they are converted into derivatives of type **60**. The ^{1}H NMR spectra of the bases **52** and **61** confirm their aromaticity [23].

Treatment of the salt **55c** with acetic anhydride or methyl chloroformate in the presence of triethylamine gave the corresponding derivatives **62a**,**b** [73, 76]. Acylation of the base **52a** with acetic anhydride or benzoyl chloride in pyridine led to the products **62a**,**c** respectively [23].

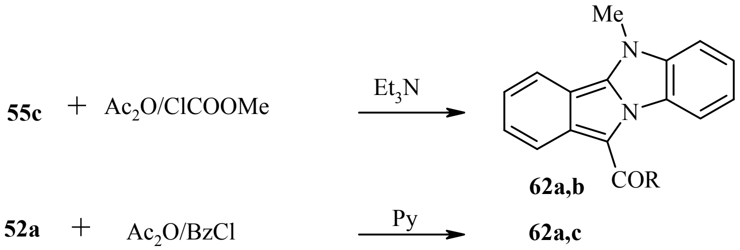


52a,b

52 a R = Me, **b** R = Et



16 **61**



62 a R = Me, **b** R = OMe, **c** R = Ph

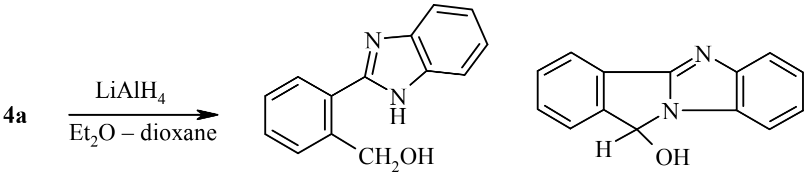
The latter had extremely low frequencies for the vibrations of the carbonyl group in the IR spectra [73].

3.1.5. Ligand Characteristics. The condensation of phthalic aldehyde with the diamine **1a** in the presence of Ni(II) gave blue complexes [77]. The general formula of the complexes is ML_2X_2, where M is a divalent metal (Ni, Co, Cu, Zn), L is the molecule of (**a**, and X represents anions of the Hal^-, NO_3^-, and SCN^- type [77, 78].

3.2. 11H-Isoindolo[2,1-*a*]benzimidazol-11-ones

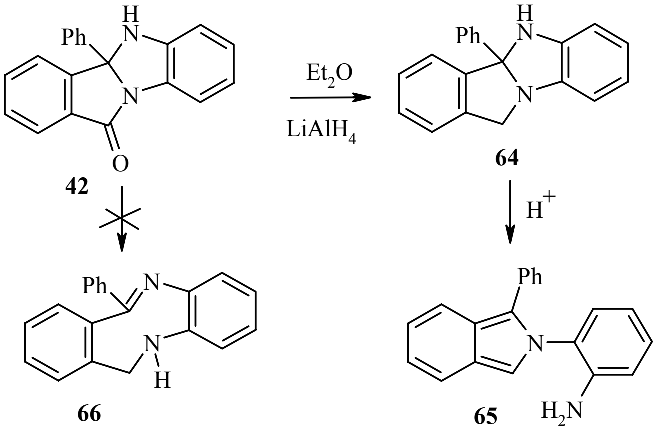
3.2.1. Basic Characteristics. 11H-Isoindolo[2,1-*a*]benzimidazole-11-one **4a** has basic characteristics; it is protonated by sulfuric acid with the formation of the salt **54a**, and with dimethyl sulfate it forms the quaternary salt **54b** [68].

3.2.2. Reactions at the Carbonyl Group. The formation of two products is possible during the reduction of compound **4a** with lithium aluminum hydride [11, 12, 22, 79, 80]. Thus, only the alcohol **6** was obtained during the reaction in a mixture of ether and dioxane [11, 12]. Under other conditions it is possible to obtain either the same product **6** (**4a**:$LiAlH_4$ = 1:1.15, yield 76%) or the carbinolamine **63** (**4a**:$LiAlH_4$ = 1:0.77, low yield) [80].

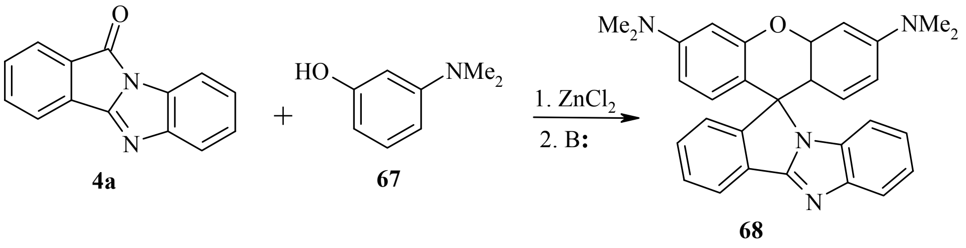


6 **63**

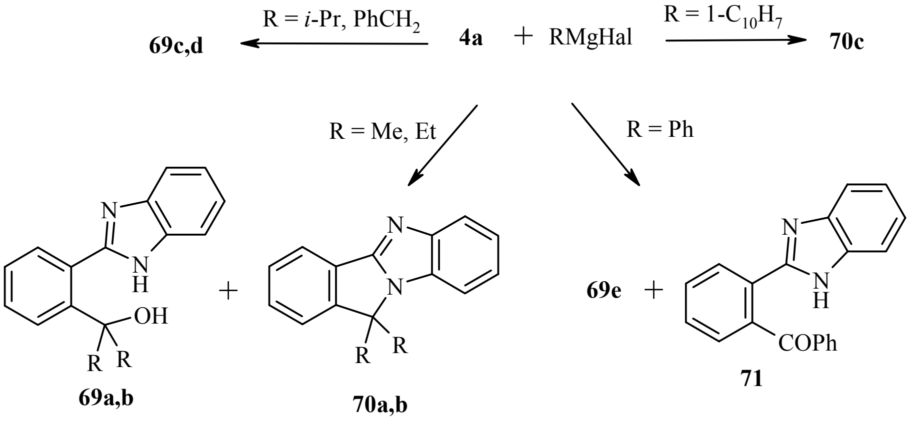
The reduction of compound **42** (R = Ph) with lithium aluminum hydride in diethyl ether [81, 82] gave an oil, which was transformed into a crystalline substance when dissolved in ethanol or chloroform. It was found that the oil has the structure **64** [81] and readily undergoes acid-catalyzed isomerization to the thermodynamically more stable isoindole **65**. Earlier the structure **66** was proposed for the product from reduction of above-mentioned compound **42** [83].



The spiroxanthene **68** was obtained as a result of the reaction of compound **4a** with *m*-(dimethylamino)phenol **67** [84].



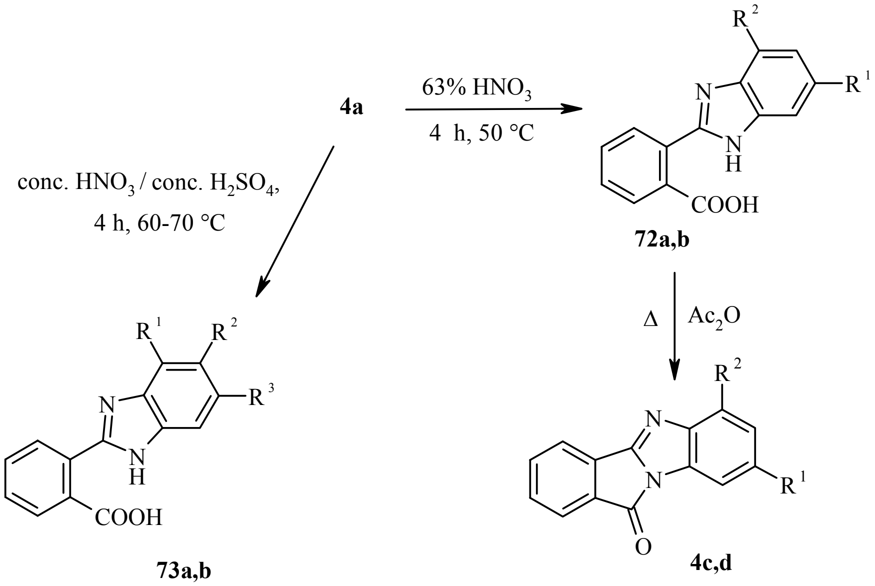
During the action of Grignard reagents RMgHal on the isoindolobenzimidazole **4a** one or two molecules of the reagent are added to it with the formation of products with structures depending on R (see the scheme).



69, 70 a R = Me, **b** R = Et; **69 c** R = *i*-Pr; **d** R = CH_2Ph; **e** R = Ph; **70c** R = $C_{10}H_7$

With R = Me and Et the alcohols **69a**,**b** (yields 96 and 76% respectively) and the disubstituted isoindolobenzimidazoles **70a**, **b** (yields 1 and 22% respectively) were obtained. The reaction of compound **4a** with isopropyl- and benzylmagnesium bromides led only to the alcohols **69c**,**d** (yields 25 and 41% respectively). In the case of 1-naphthylmagnesium bromide the base 7**0c** (R = 1-$C_{10}H_7$) was obtained with a yield of 6%, and with PhMgBr the alcohol **69e** (37%) and the ketone **71** (25%) were formed [85].

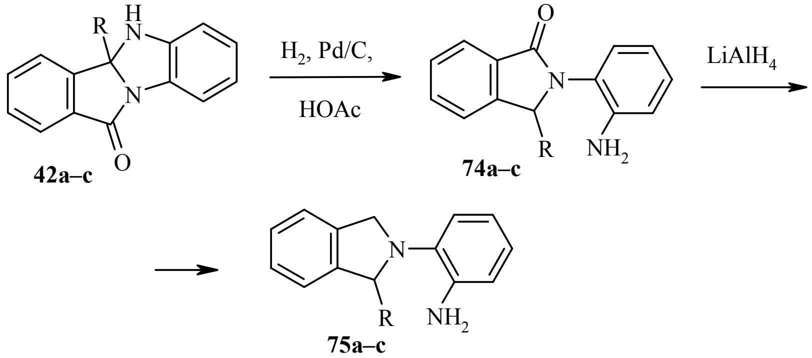
3.2.3. Nitration. The nitration of the isoindolobenzimidazole **4a** with nitric acid takes place at the benzimidazole fragment and is accompanied by opening of the lactam ring, leading to the formation of mono- and dinitro-substituted 2-benzimidazolylbenzoic acids **72** and **73** respectively. Under comparatively mild conditions (63% HNO_3) the 6'-substituted acid **72a** is mostly formed. If the conditions are changed (with HNO_3–H_2SO_4 and HNO_3–Ac_2O mixtures and conc. HNO_3) the reaction mixture contains the 4'-nitro acid (**72b**) as impurity. Under severe conditions the 5',6'-dinitro derivative **73a** is the major product, and the 4',6'-disubstituted acid **73b** is the minor product. When compounds **72a**,**b** were heated in acetic anhydride the corresponding cyclization products 6- and 8-nitro-substituted isoindolobenzimidazolones **4c**,**d** were obtained [86].



4c, **72a** $R^1 = H$, $R^2 = NO_2$; **4d**, **72b** $R^1 = NO_2$, $R^2 = H$;
73 a $R^1 = H$, $R^2 = R^3 = NO_2$, **b** $R^1 = R^3 = NO_2$, $R^2 = H$

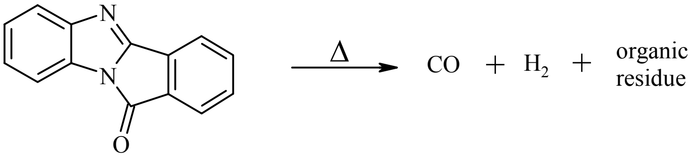
3.2.4. Opening the Lactam Ring. The examples examined in sections 3.2.2 and 3.2.3 show that the lactam ring in the isoindolo[2,1-*a*]benzimidazol-11-one system **4a** is a labile unit and is readily opened during various transformations. It is known that opening occurs even under the influence of traces of water [28], and this has been used in the synthesis of the corresponding 2-benzimidazolylbenzoic acids of type **31** [87].

3.2.5. Cleavage in the Imidazole Ring. The imidazole ring of substituted isoindolo[2,1-*a*]-benzimidazol-11-ones **42** can be cleaved as a result of hydrogenolysis. The obtained 2-(2-aminophenyl)phthalimidines **74** can then be used for the production of 2-(2-aminophenyl)isoindolines **75** [88].

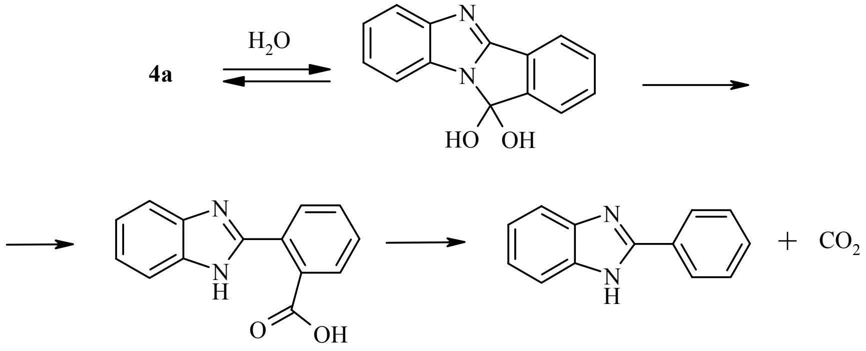


42, 74, 75 **a** R = Me, **b** R = Et, **c** R = Ph

3.2.6. Thermal Decomposition. During study of the thermal decomposition of compounds containing the structural unit of isoindolo[2,1-*a*]benzimidazole-11-one **4a** [89-93] it was established [92] that compound **4a** begins to decompose at 490°C (with the release of CO and H_2). (The structure of the obtained organic residue was not indicated.)



In [93] the effect of moisture on the thermal decomposition of compound **4a** was studied, and it was shown that heterolytic dissociation of the C–N bond in the N–C=O fragment is accelerated in the presence of water and takes place at 350-450°C (see the scheme below).



Schemes for the decomposition were proposed using the extended Hückel method [94].

4. APPLICATIONS

Cyanine dyes of the isoindolo[2,1-*a*]benzimidazole series have been proposed as sensitizers for the silver halide emulsions in negative photographic materials [95] and also for the application of orange-yellow colors to modified polyacrylonitrile fibers [96].

The polymers examined above – pyrrones – are the most widely used among compounds containing an isoindolobenzimidazole fragment. Pyrrones represent an extensive group of high-molecular compounds with unique characteristics. They are used in such regions of technology as aircraft and spacecraft construction [97, 98], atomic energy, and electronics. They are heat-resistant, nonmelting, and suitable for use at 300°C and above. The polymer only begins to lose weight at 450°C [94, 100]. Pyrrones are characterized by strong ablative characteristics. The strength of the pyrrone films does not deteriorate after irradiation with electrons with energies of 2-3 MeV at a radiation dose of 10000 Mrad, whereas polyester films are destroyed at a dose of 200 Mrad [61, 100, 101].

Apart from the polymeric materials, low-molecular compounds based on the isoindolobenzimidazolone molecule **4a** have also found widespread application. Thus, substituted compounds **4a** are used as dyes for various fibers [102] or as pigments for plastics [28]. During polymerization in the presence of such compounds polyamide films have increased resistance to photo- and thermooxidative degradation [103]. A series of dyes have been synthesized on the basis of reaction of the diamine **1a** with nitro- and acylamino [82, 104], hydroxy [104], tetrachloro [105-107], and tetrabromo [34, 108, 109] derivatives of phthalic anhydride. The bisproducts from the condensation of 3,3'-diaminobenzidine with phthalic anhydride [110] and of pyromellitic anhydride with *o*-phenylenediamine [111] and bisproducts of type **37** (R = H [40] or R = NO_2 [41]) can be used as dyes (see section 1.2.1). An azo dye based on 11H-7-amino-2-chloroisoindolo[2,1-*a*]benzimidazol-11-one is known [112]. The synthesis of azo pigments containing the isoindolobenzimidazole system **4a** has been described [113].

The creation of electrophotographic photoconductors containing azo dyes based on compound **4a** was reported in [114-116]. Derivatives of the latter can be used in electroluminescent elements [117] and electrostatographic toners]118]; fluorescent materials based on them were also created [119-121].

5. BIOLOGICAL ACTIVITY

During study of the biological activity of derivatives of isoindolo[2,1-*a*]benzimidazolone **4a** it was shown that compounds **42** have sedative, tranquillizing, and antidepressant activity [47, 49, 82].

Derivatives of isoindolo[2,1-*a*]benzimidazole exhibit low cytotoxic activity [27].

6. ADDENDUM

While the review was being edited and revised new data appeared on the chemistry of isoindolobenzimidazole. Thus, the synthesis of new derivatives of 11H-isoindolo[2,1-*a*]benzimidazolones [122-124] and the production of the partially saturated analogs of these compounds of type **44** [125, 126] were described. In [127] the fluorescent characteristics of various derivatives of isoindolobenzimidazolones are examined.

It is also necessary to mention papers on the practical application of isoindolo[2,1-*a*]benzimidazole derivatives as electrophotographic photoreceptors [128-130] and as additives for polymers [131]. Fluorescent compositions based on isoindolobenzimidazolone are described in the patent [132]. Additional data on the biological activity can be found in [133-137].

REFERENCES

1. F. S. Babichev, V. A. Kovtunenko, and A. K. Tyltin, *Uspekhi Khimii,* **50**, 2073 (1981).
2. V. A. Kovtunenko and Z. V. Voitenko, *Russ. Chem. Rev.*, **63**, 997 (1994).

3. F. S. Babichev and V. A. Kovtunenko, *Chemistry of Isoindole* [in Russian], Naukova Dumka, Kiev (1983).
4. Z. V. Voitenko, T. V. Egorova, and V. A. Kovtunenko, *Khim. Geterotsikl. Khim.*, 1171 (2002). [*Chem. Heterocycl. Comp.*, **38,** 1019 (2002)].
5. A. A. Pokhodenko, Z. V. Voitenko, and V. A. Kovtunenko, *Uspekhi Khimii,* **73**, 833 (2004).
6. J. Thiele and K. G. Falk, *Liebigs Ann. Chem.*, **347**, 112 (1906).
7. W. L. Mosby, *Heterocyclic Systems with Bridgehead Nitrogen Atoms*, Intersci. Publ., Inc., New York; Intersci. Publ. Ltd., London (1961), Pt. 1 – 2 (*A series of monographs*, A. Weissberger, *The Chemistry of Heterocyclic Compounds*).
8. W. H. Ried and Bodem, *Chem. Ber.*, **89**, 708 (1956).
9. W. Ried and E. Torinus, *Chem. Ber.*, **92**, 2902 (1959).
10. V. Anger, *Oesterr. Chem. Ztg.*, **62**; 352 (1961); *Chem. Abstr.*, **56**, 57141 (1962).
11. F. Sparatore and G. Bignardi, *Atti Acad. Ligure Sci. Lett. (Genoa)*, **19**, 137 (1962).
12. F. Sparatore and G. Bignardi, *Gazz. Chim. Ital.*, **92**, 606 (1962).
13. D. Amos and R. G. Gillis, *Austral. J. Chem.*, **17**, 1440 (1964).
14. H. D. Perlmutter and P. S. Knapp, *J. Org. Chem.*, **32**, 2350 (1967).
15. T. Amano and T. Sakano, *Yakugaku Zasshi*, **90**, 1 (1970); *Chem. Abstr.*, **72**, 74567 (1970).
16. W. Ried and H. Kohl, *Liebigs Ann. Chem.*, **734**, 203 (1970).
17. M. K. Eberle, W. J. Houlihan, and P. Schirm, *J. Org. Chem.*, **38**, 3872 (1973).
18. C. Tamborski, U. D. G. Prabhu, and K. C. Eapen, *J. Fluorine Chem.*, **28**, 139 (1985).
19. F. S. Babichev, A. K. Tyltin, and L. I. Shevchuk, *Ukr. Khim. Zh.,* **37**, 916 (1971).
20. P. E. Cassidy, R. J. Wallace, and T. M. Aaminabhavi, *Polymer*, **27**, 1131 (1986).
21. M. Yu. Kornilov, A. K. Tyltin, A. V. Turov, and F. S. Babichev, *Ukr. Khim. Zh.,* **41**, 390 (1975).
22. G. Irick, Jr., *J. Heterocycl. Chem.*, **7**, 33 (1970).
23. F. S. Babichev and L. G. Khil'ko, *Ukr. Khim. Zh.,* **40**, 946 (1974).
24. A. H. Bedair, R. Q. Lamphon, and S. A. Ghazal, *J. Chem. Pak.*, **10**, 404 (1988); *Chem. Abstr.*, **112**, 20869 (1990).
25. D. B. Reuschling and F. Kröhnke, *Chem. Ber.*, **104**, 2103 (1971).
26. E. Müller and G. Zoutas, *Chem. Ber.*, **105**, 2529 (1972).
27. S. K. Meegalla, J. G. Stevens, C. A. McQueen, A. Y. Chen, and C. Yu, *J. Med. Chem.*, **37**, 3434 (1994).
28. I. Arient, *Uspekhi Khimii,* **34**, 1908 (1965).
29. P. R. Young, *J. Heterocycl. Chem.*, **9**, 371 (1972).
30. J. Arient and J. Marchan, *Collect. Czech. Chem. Comm.*, **26**, 98 (1961).
31. J. G. Colson, R. H. Michel, and R. M. Paufler, *J. Polym. Sci., Polymer Chemistry Ed.*, **4**, 59 (1966); *Chem. Abstr.*, **64**, 68266 (1966).
32. F. Dawans and C. S. Marvel, *J. Polym. Sci.*, **A3**, 3549 (1965); *Chem. Abstr.*, **64**, 11781 (1966).
33. A. C. Ranade and J. Gopal, *J. Chem. Ind. (London)*, **15**, 582 (1978).
34. K. Watanabe and H. Harada, Jpn. Pat. 76123224; *Chem. Abstr.*, **86**, 56755 (1977).
35. H. Al-Khathlan and H. Zimmer, *J. Heterocycl. Chem.*, **25**, 1047 (1988).
36. V. V. Korshak, G. L. Berestenova, Yu. E. Doroshenko, L. V. Postinova, and V. A. Khomutov, *Izv. Akad. Nauk SSSR. Ser. Khim.,* 422 (1978).
37. M. I. Dovgosheya and B. M. Krasovitskii, *Zh. Org. Chim.*, **2**, 1288 (1966).
38. A. Mukherjee, M. S. Akhar, V. L. Sharma, M. Seth, A. P. Bhaduri, A. Agnihotri, P. K. Mehrota, and V. P. Kamboj, *J. Med. Chem.*, **32**, 2297 (1989).
39. M. Suzuki, E. Hosokawa, S. Hirada, and T. Hoshiro, Jpn. Pat. 771560, *Chem. Abstr.*, **87**, 135332 (1977).
40. V. V. Korshak, A. L. Rusanov, I. Ya. Kolontarov, F. F. Niezi, and I. Batirov, *Dokl. Akad. Tadz. SSR*, **18**, 26 (1975).

41. Badische Anilin & Soda Fabrik-AG, Fr. Pat.1564233; *Chem. Abstr.*, **73**, 110904 (1970).
42. J. Preston and W. F. Dewinter, *J. Heterocycl. Chem.*, **7**, 433 (1970).
43. M. Suzuki and E. Hosokawa, Jpn. Pat. 7027819; *Chem. Abstr.*, **74**, 42878 (1971).
44. N. N. Voznesenskaya, V. N. Yarosh, É. N. Teleshov, and A. N. Pravednikov, *Vysokomol. Soedin.*, **13**, 140 (1976).
45. S. A. Siling, I. I. Ponomarev, N. I. Vasyukova, V. V. Korshak, and S. V. Vinogradova, *Izv. Akad. Nauk SSSR. Ser. Khim.,* 2335 (1980).
46. P. Aeberli, and W. J. Houlihan, *J. Org. Chem.*, **33**, 2402 (1968).
47. J. R. Geigy, Belg. Pat. 659530; *Chem. Abstr.*, **64**, 6665 (1966).
48. J. A. Hadfield, V. H. Pavlidis, and J. R. A. Roffey, *Synth. Commun.*, **25**, 1319 (1995).
49. W. J. Houlihan, US Pat. 3329684; *Chem. Abstr.*, **67**, 108656 (1967).
50. W. J. Houlihan, US Pat. 3372166; *Chem. Abstr.*, **69**, 36113 (1968).
51. P. Louvet, F. Thomasson, and L. D. Cong, *J. Heterocycl. Chem.*, **31**, 39 (1994); *Chem. Abstr.*, **121**, 35542 (1994).
52. G. Stajer, F. Csende, G. Bernath, and P. Sohar, *Heterocycles*, **37**, 883 (1994).
53. R. Sillanpaeae, F. Csende, and G. Stayer, *Acta Crystallogr.*, **C51**, 2169 (1995); *Chem. Abstr.*, **123**, 326239 (1995).
54. T. S. Sulkowski and A. A. Mascitti, US Pat. 3936471; *Chem. Abstr.*, **84**, 435669 (1976).
55. T. Nakano and A. Martin, *J. Heterocycl. Chem.*, **16**, 1235 (1979).
56. J. Huang and M.-M. Gu, *Youji Huaxue*, **14**, 604 (1994); *Chem. Abstr.*, **122**, 214000 (1995).
57. S. Eguchi, Y. Matsushita, and H. Takauchi, *J. Org. Chem.*, **57**, 6975 (1992).
58. V. L. Bell and G. E. Pezdirtz, *J. Polym. Sci.*, **B3**, 977 (1965); *Chem. Abstr.*, **64**, 44255 (1966).
59. A. L. Berlin, B. I. Liogon'kii, and G. M. Shamraev, *Uspekhi Khimii,* **40**, 511 (1971).
60. B. A. Zhurbanov, Z. Kh. Azimov, and Zh. Kh. Ibrasheva, in: *Chemistry and Chemical Technology* [in Russian] (1973), No. 14, p. 3; *Chem. Abstr.*, **83**, 98263 (1975).
61. L. M. Levites, M. V. Shablygin, T. V. Kravchenko, G. I. Kudryavtsev, L. V. Goncharova, and A. I. Koretskaya, *Vysokomol. Soedin.*, **B18**, 459 (1976).
62. I. B. Rabinovich, A. L. Rusanov, and N. V. Karyakin, *Vysokomol. Soedin.*, **A15**, 360 (1973).
63. I. B. Rabinovich, A. N. Mochalov, L. I. Pavlinov, V. V. Korshak, A. L. Rusanov, and R. D. Katsarova, *Dokl. Akad. Nauk*, **198**, 597 (1971).
64. V. A. Kovtunenko, Z. V. Voitenko, V. L. Sheltun, L. I. Savranskii, A. K. Tyltin, and F. S. Babichev, *Khim. Geterotsikl. Khim.*, 646 (1987). [*Chem. Heterocycl. Comp.*, **23**, 535 (1987)].
65 V. V. Korshak, A. L. Rusanov, A. I. Bolduzev, V. A. Kosobutskii, V. A. Belyakov, M. K. Kereselidze, and T. V. Lekae, *Izv. Akad. Nauk SSSR. Ser. Khim.,* 563 (1983).
66. E. Maki, F. Csende, G. Stajer, P. Vainiotalio, and K. Pihalaja, *Rapid Commun. Mass. Spectrom.*, **8**, 858 (1994); *Chem. Abstr.*, **122**, 105119 (1995).
67. B. K. Manukian, *Helv. Chim. Acta*, **48**, 1999 (1965).
68 A. I. Kiprianov and V. A. Shrubovich, *Zh. Obshch. Khim.*, **30**, 3746 (1960).
69. R. L. Sharma, M. Kumari, N. Kumar, and B. K. Sharma, *J. Heterocycl. Chem.*, **8**, 155 (1998); *Chem. Abstr.*, **130**, 237516 (1999).
70 H. Z. Alkhathlan and H. A. Al-Lohedan, *J. Chem. Res., Synop.*, **1**, 10 (1995); *Chem. Abstr.*, **122**, 213464 (1995).
71. B. Lal and A. P. Bhaduri, *Indian J. Chem.*, **15B**, 359 (1977).
72. F. S. Babichev, L. G. Khil'ko, and N. V. Mel'nichenko, *Ukr. Khim. Zh.,* **35**, 615 (1969).
73. W. J. Salmond, *Tetrahedron Lett.*, **47**, 4689 (1967).
74. F. S. Babichev and L. G. Khil'ko, *Visnik Kiiv. Un-tu. Ser. Khimi*, **17**, 29 (1976); *Ref. Zh. Khim.*, 1Zh242 (1978).

75. F. S. Babichev, *Acta Univ. Debrecen. Ser. Phys. et Chim.*, **12**, 73 (1966).
76. D. V. Bite and A. K. Aren, *Khim. Geterotsikl. Khim.*, 1083 (1969). [*Chem. Heterocycl. Comp.*, **5**, 820 (1969)].
77. M. S. Elder, G. A. Melson, and D. H. Brusch, *Inorg. Chem.*, **5**, 74 (1966).
78. G. A. Melson and R. H. Nuttall, *J. Mol. Struct.*, **1**, 405 (1968).
79. J. Arient, L. Havličkova, and J. Šlosar, *Collect. Czech. Chem. Commun.*, **29**, 3115 (1964).
80. J. Arient and L. Havličkova, *Collect. Czech. Chem. Communs.*, **28**, 1885 (1963).
81. P. Aeberli and W. J. Houlihan, *J. Org. Chem.*, **34**, 1720 (1969).
82. W. J. Houlihan, US Pat. 3428650; *Chem. Abstr.*, **70**, 77785 (1973).
83. T. S. Sulkowski, Belg. Pat. 646221; *Chem. Abstr.*, **63**, 54735 (1965).
84. S. Gunzenhauser, B. Hellrung, and B. Heinz, *Helv. Chim. Acta*, **62**, 171 (1979).
85. J. Arient, J. Šlosar, L. Havličkova, J. Knižek, *Collect. Czech. Chem. Communs.*, **31**, 4682 (1966).
86. J. Arient, J. Šlosar, and L. Havličkova, *Collect. Czech. Chem. Communs.*, **30**, 1913 (1965).
87. J. S. Baum and T. M. Chen, US Pat. 4623379; *Chem. Abstr.*, **106**, 45729 (1987).
88. T. S. Sulkowski and A. A. Mascitti, US Pat. 3466297; *Chem. Abstr.*, **71**, 112810 (1969).
89. V. V. Korshak, S. A. Pavlova, P. N. Gribkova, L. A. Mikadze, and A. L. Rusanov, *Izv. Akad. Nauk Gruz. SSR. Ser. Khim.*, **2**, 313 (1976).
90. D. M. Mognonov, J. Varga, A. I. Batotsyrenova, V. G. Samsonova, and A. A. Izyneev, *J. Therm. Anal.*, **30**, 1053 (1985); *Chem. Abstr.*, **104**, 130403 (1986).
91. V. V. Korshak, S. A. Pavlova, P. N. Gribkova, L. A. Mikadze, A. L. Rusanov, L. Kh. Plieva, and T. V. Lekae, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1381 (1977).
92. D. M. Mognonov, V. A. Khomutov, A. A. Izyneev, and Yu. E. Doroshenko, *Izv. Sibirsk. Otd. Akad. Nauk. SSSR. Ser. Khim. Nauk*, **2**, 124 (1978).
93. V. V. Korshak, S. A. Pavlova, P. N. Gribkova, I. V. Vlasova, A. L. Rusanov, and V. V. Rodé, *Dokl. Akad. Nauk*, **206**, 359 (1972).
94. O. B. Tomilin and I. V. Stankevich, *Izv. Akad. Nauk SSSR. Ser. Khim.,* 1275 (1977).
95. L. G. S. Brooker and G. L. Oliver, US Pat. 3600184; *Chem. Abstr.*, **75**, 152989 (1971).
96. G. Irick, US Pat. 3531478; *Chem. Abstr.*, **74**, 55145 (1971).
97. P. Fajet, *Rev. Gen. Caoutch. Plast.*, **54**, 65 (1977); *Chem. Abstr.*, **87**, 118911 (1977).
98. B. G. Kimmel and L. E. Karre, *NASA Contract. Rep.*, NASA-CR-1791 (1971); *Chem. Abstr.*, **76**, 34776 (1972).
99. E. P. Krasnov, V. P. Aksenova, A. A. Belyaev, A. V. Volokhina, G. I. Kudryavtseva, V. M. Savinova, and V. I. Terenkin, *Vysokomol. Soedin.*, **15**, 1606 (1973).
100. H. Ahne, E. Kuehn, and R. Rubner, Ger. Pat. 2933819; *Chem. Abstr.*, **94**, 209479 (1981).
101. H. L. Price and V. L. Bell, *Symp. Exhib., 15th*, 335 (1969); *Chem. Abstr.*, **72**, 122336 (1970).
102, M. Groll, V. Hederich, and H. Bien, Ger. Pat. 2424542; *Chem. Abstr.*, **84**, 91652 (1976).
103. I. Ya. Kolontarov, F. F. Niyazi, and Yu. V. Chajko, *Int. J. Polym. Mat.*, **13**, 53 (1990); *Chem. Abstr.*, **114**, 166182 (1991).
104. J. Dassigny and J. Robin, Fr. Pat. 1111620; *Chem. Abstr.*, **53**, 102815 (1959).
105. B. M. Krasovitskii and E. F. Kravchenko, *Zh. Prikl. Khim.*, **35**, 1604 (1962).
106. D. W. Hein, R. J. Alheim, M. Borough, and J. J. Leavitt, US Pat. 2985661.
107. E. E. Jaffer, Eur. Pat. 456609; *Chem. Abstr.*, **116**, 13153 (1992).
108. Badische Anilin & Soda-Fabrik AG, Fr. Pat. 1576459; *Chem. Abstr.*, **73**, 67698 (1970).
109. Badische Anilin & Soda-Fabrik AG, Brit. Pat. 1173412; *Chem. Abstr.*, **73**, 46681 (1970).
110. R. Jean, Fr. Pat. 1090115; *Chem. Abstr.*, **53**, 48125 (1959).
111. B. K. Manukian, *Helv. Chim. Acta*, **47**, 2211 (1964).

112. K. M. Patel, V. H. Patel, M. P. Patel, and R. G. Patel, *Dyes and Pigments*, **55**, 53 (2002); *Chem. Abstr.*, **138**, 97382 (2003).
114. Y. Kaghizaki, Jpn. Pat. 0339751; *Chem. Abstr.*, **116**, 31312 (1992).
113. M. Shigemitsu, T. Kumano, M. Hikasaka, and Y. Kameyama, Jpn. Pat. 7416252; *Chem. Abstr.*, **82**, 45214 (1975).
115. Y. Kaghizaki and H. Takai, Jpn. Pat. 02156249; *Chem. Abstr.*, **114**, 111876 (1991).
116. M. Okaji, K. Enomoto, A. Ito, and K. Haino, Jpn. Pat. 02291564; *Chem. Abstr.*, **115**, 18587 (1991).
117. T. Enokida and Y. Suda, Jpn. Pat. 06228546; *Chem. Abstr.*, **122**, 42894 (1995).
118. Orient Chemical Industries, Ltd., Jpn. Pat. 59185349; *Chem. Abstr.*, **102**, 176456 (1985).
119. J. Otani, K. Kunimoto, T. Deno, B. G. Delvin, and K. Kodoma, WO Pat. 9833862; *Chem. Abstr.*, **129**, 195610 (1998).
120. B. G. Delvin, J. Otani, K. Kunimoto, A. Iqubal, S. H. Eldin, WO Pat. 9833866; Chem. Abstr., 129, 195611 (1998).
121. B. G. Delvin, J. Otani, K. Kunimoto, T. Deno, A. Iqubal, and S. H. Eldin, WO Pat. 9833864; *Chem. Abstr.*, **129**, 181897 (1998).
122. B. P. V. Lingaiah, T. Yakaiah, P. S. Rao, and B. Narsaiah, *Heterocycles*, **65**, 2329 (2005).
123. A. Cul, A. Daich, B. Decroix, G. Sanz, and L. Van Hijfte, *Tetrahedron*, **60**, 11029 (2004).
124. K. L. Tan, R. G. Bergman, and J. A. Ellman, *J. Am. Chem. Soc.*, **123**, 2685 (2001).
125. F. Miklós, I. Kanizsai, S. Thomas, E. Kleinpeter, R. Sillanpää, and G. Stájer, *Heterocycles*, **63**, 63 (2004).
126. F. Miklós, A. Hetenyi, P. Sohar, and G. Stájer, *Monatsh. Chem.*, **135**, 839 (2004).
127. J. Otani, H. Yamamoto, M. Fukuda, and K. Kodama, *J. Luminescence*, **104**, 273 (2003); *Chem. Abstr.*, **139**, 298503 (2003).
128. Y. Kitahara and T. Shibata, Jpn. Pat. 2002341566; *Chem. Abstr.*, **137**, 391026 (2002).
129. Y. Komai and M. Shoji, Jpn. Pat. 2003228186; *Chem. Abstr.*, **139**, 171237 (2003).
130. Y. Komai, M. Shoji, H. G. Li, and M. Sasaki, Jpn. Pat. 2003207914; *Chem. Abstr.*, **139**, 140901 (2003).
131. Y. Meng, I. A. Abu-Yousef, A. R. Hlil, and A. S. Hay, *Macromolecules*, **33**, 9185 (2000).
132. B. G. Devlin, J. Otani, K. Kunimoto, T. Deno, A. Iqbal, and S. H. Eldin, US Pat. 6080516; *Chem. Abstr.*, **133**, 81564 (2000).
133. S. Bond, V. A. Sanford, J. N. Lambert, C. Y. Lim, J. P. Mitchell, A. G. Draffan, and R. H. Nearn, WO Pat. 2005061513; *Chem. Abstr.*, **143**, 115538 (2005).
134. B. L. Khatri, T. A. Upadhyay, A. M. Trivedi, V. Sodha, and H. H. Parekh, *J. Inst. Chem.*, **74**, 205 (2002); *Chem. Abstr.*, **139**, 395858 (2003).
135. W. J. Houlihan, U. F. Ahmad, J. Koletar, L. Kelly, L. Brand, and T. A. Kopajtic, *J. Med. Chem.*, **45**, 4110 (2002).
136. T. Iino, M. Bamba, J. Eiki, and T. Nagase, WO Pat. 2002066479; *Chem. Abstr.*, **137**, 201333 (2002).
137. R. Doshi, P. Kagthara, and H. H. Parekh, *J. Inst. Chem.*, **72**, 140 (2000); *Chem. Abstr.*, **135**, 5563.