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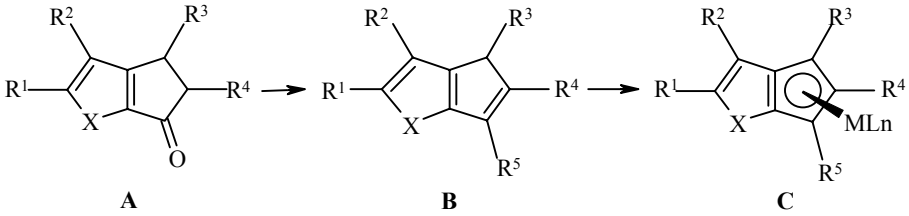
CYCLOPENTADIENES ANNELATED WITH FIVE-MEMBERED HETEROCYCLES: METHODS OF SYNTHESIS, HETEROORGANIC DERIVATIVES, AND SYNTHETIC PRECURSORS. (REVIEW)

I. P. Laishevtsev, I. A. Kashulin, I. V. Taidakov, V. V. Bagrov, and I. E. Nifant'ev

The review is devoted to cyclopentadienes annelated with five-membered heterocycles (furan, pyrrole, thiophene, and their benzo analogs) (hetarenocyclopentadienes), their heteroorganic derivatives, and the synthetic precursors (hetarenocyclopentanones).

Keywords: hetarenocyclopentadienes, hetarenocyclopentanones, dithiophenocyclopentadienes, heteroorganic derivatives, intramolecular cyclization, reduction.

Substituted cyclopentadienes and their benzocondensed derivatives (indenes and fluorenes) [1, 2] are widely used in heteroorganic chemistry as ligands in the synthesis of organometallic compounds. Cyclopentadiene derivatives where the cyclopentadienyl ring is annelated with a five-membered heterocycle of the thiophene series, which for concision we will call hetarenopentalenes **B** (X = O, S, NR), have recently begun to attract the constant attention of chemists.



The interest in compounds **B** and in the complexes **C** based on them is explained by the fact that π-excessive thiophene, pyrrole, and furan exhibit electron-donating characteristics, greatly surpassing the electron-donating characteristics of the usual hydrocarbon substituents. As a consequence the organometallic derivatives of heterocyclic cyclopentadienes demonstrate chemical and catalytic characteristics substantially differing from the characteristics of the usual cyclopentadienyl derivatives.

Their use in the production of metallocene catalysts for the polymerization of olefins may become an important application of compounds **B**. Recently it was shown that one of the main factors affecting the activity of metallocene catalysts is the electron-donating character of the cyclopentadienyl ligand. This is why titanium and zirconium complexes based on compounds **B** may have extremely high activity in the polymerization of olefins. Results on the application of heterocyclic metallocenes in such processes are extremely encouraging.

M. V. Lomonosov Moscow State University, Moscow 119992, Russia; e-mail: inif@org.chem.msu.ru, ilai@org.chem.msu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 643-679, May, 2003. Original article submitted September 10, 2001.

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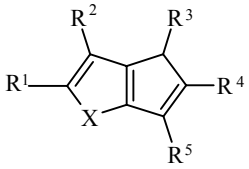
Further progress in the study and application of the complexes **C** is limited by the small degree of study of the cyclopentadienes **B**. At the present time information on such compounds and also their heteroorganic derivatives has been fragmentary. In view of the importance of compounds **B** and **C** for organometallic chemistry at the present time and in the future and also the complete lack of any reviews on the subject we have assembled and analyzed all the currently available information on cyclopentadienes **B**. In this review we will examine the principal synthetic approaches to the production both of cyclopentadienes condensed with furan, pyrrole, and thiophene and of the currently known organometallic derivatives.

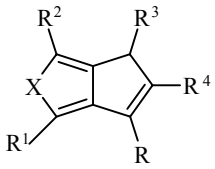
Most of the cyclopentadienes **B** were obtained from the corresponding cyclic ketones **A**. Unlike the cyclopentadienes **B**, the ketones **A** have been investigated in a relatively large amount of detail due to the fact that many of them exhibit clearly defined biological activity.

1. SYNTHESIS OF CYCLOPENTADIENES CONDENSED WITH FIVE-MEMBERED HETEROCYCLES AND THEIR BENZANNELATED DERIVATIVES

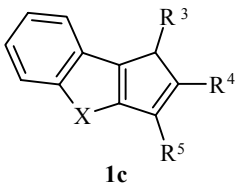
Compounds **1a-c** (X = O, S, NR) can be regarded as heteroanalogs of indene and in this connection are of interest in the synthesis of heteroorganic compounds. Most of the papers in this field have been devoted to thiapentalenes and azapentalenes, whereas the synthesis and characteristics of oxapentalenes have been investigated very little on account of the difficulty of synthesizing them.



1a



1b



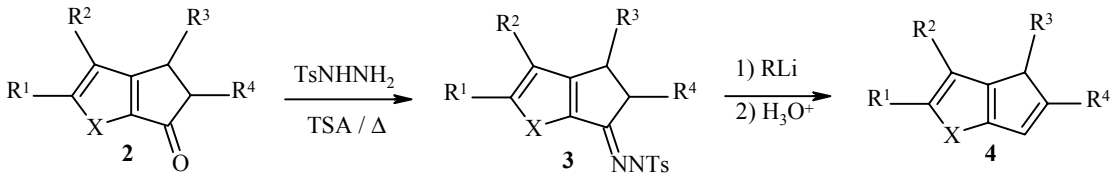
1c

In the overwhelming majority of cases the hetarenopentalenes were obtained from cyclic ketones of type **A**. There are only a limited number of methods that make it possible to obtain hetarenopentalenes without using the respective ketones, and the methods in this case involve photochemical or thermal rearrangements [3].

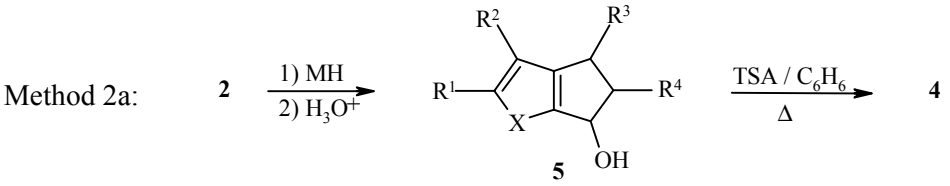
1.1. Synthesis of Hetarenopentalenes

Two main methods have been described for transforming hetarenocyclopentanones into the required pentalenes. Method 1 involves the transformation of hetarenocyclopentanones into tosylhydrazones and treatment of the latter with alkyllithium followed by hydrolysis of the lithium salt with the formation of a mixture of hetarenopentalenes isomeric with respect to the position of the double bond [4-7]. Method 2 involves transformation of the hetarenocyclopentanones into the corresponding alcohols either by the action of alkali-metal hydrides (method 2a) or by reaction with Grignard reagents (method 2b) and subsequent dehydration [8-10]. In all cases the yields vary from moderate to very good.

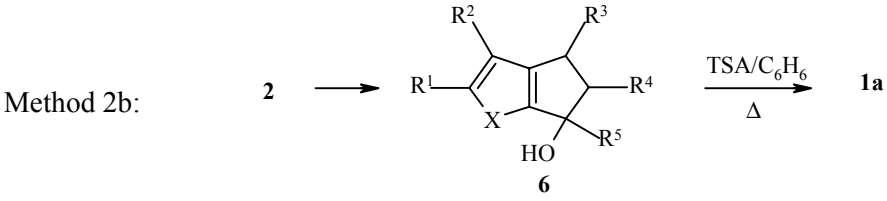
Method 1



Method 2a:



Method 2b:



1,3-Dimethyl-4H-cyclopenta[*c*]thiophene (**7**) was obtained by a rather good method with a yield of 65% [7].

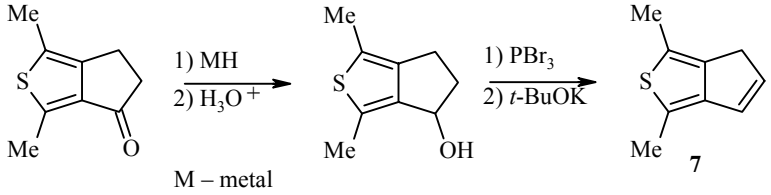


TABLE 1. The Obtained Hetarenopentalenes

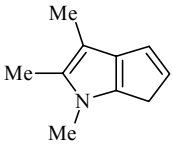
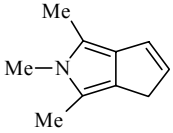
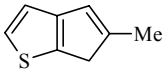
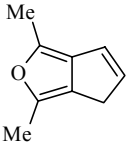
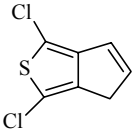
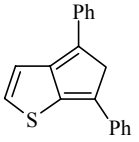
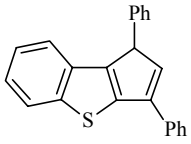
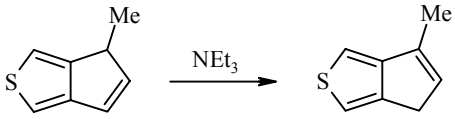
Compound		Yield, %	Method	Reference
1		2	3	4
	(**8**)	53	1	[5]
	(**9**)	87	1	[11]
	(**10**)	41 50-80	1 2a	[12]
	(**11**)	70	1	[6]
	(**12**)	80	2a	[10]

TABLE 1 (continued)

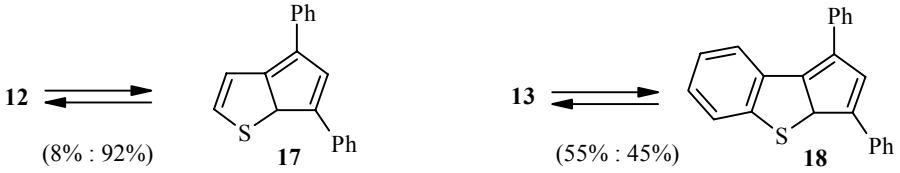
1		2	3	4
	(**13**)	78	2b	[13]
	(**14**)	80	2b	[14]

A series of papers were devoted to the tautomeric characteristics of cyclopenta[*c*]thiophenes [15, 16]. It was shown that treatment of 4-methyl-4H-cyclopenta[*c*]thiophene (**15**) with triethylamine led to a 1,3-sigmatropic shift, accompanied by migration of the double bond and the formation of 6-methyl-4H-cyclopenta[*c*]thiophene (**16**) [16].



15 **16**

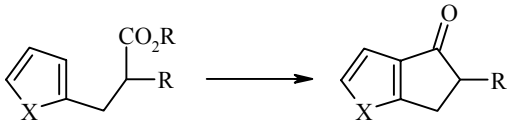
Interesting behavior was exhibited by 4,6-diphenyl-4H-cyclopenta[*b*]thiophene (**13**) and 1,3-diphenyl-1H-cyclopenta[*b*][1]benzothiophene (**14**). It was found that these compounds were in equilibrium with their isomeric 4,6-diphenyl-5H-cyclopenta[*b*]thiophenes **17** and **18** respectively, which were capable of entering into a Diels–Alder reaction. It was established by ^{1}H NMR that the fraction of 1,3-diphenyl-1H-cyclopenta[*b*][1]benzothiophene in the mixture amounted to 55% [14], while the fraction of 4,6-diphenyl-4H-cyclopenta[*b*]thiophene was only 8%. The larger content of the iso structure in the case of the benzothiapentalene derivative is due to the fact that the loss of aromaticity in the thiophene ring is compensated by the formation of the conjugated cyclopentadienyl system containing two phenyl substituents. In the case of thiapentalene the loss of the aromaticity of the thiophene has an extremely unfavorable effect, and the fraction of the iso structure is therefore extremely small.



12 (8% : 92%) **17** **13** (55% : 45%) **18**

1.2. Methods for the Synthesis of Hetarenocyclopentanones

Methods for the synthesis of cyclic ketones can be divided into general methods such as the cyclization of derivatives of 3-hetarylpropionic acids, the cyclization of hetaryl vinyl ketones, and the single-stage addition of acrylic acids, which can be applied to all five-membered π-donor heterocycles (furan, thiophene, pyrrole) and their benzannelated analogs, and special methods of synthesis applicable only to a limited range of compounds.

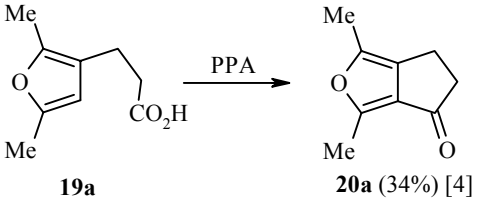


19 **20**

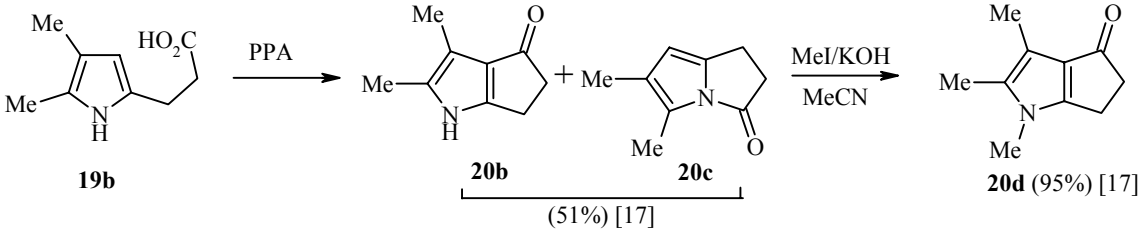
Positive aspects of the cyclization of derivatives of 3-hetarylpropionic acids (X = O, S, NR) are the relative accessibility of suitable derivatives of 3-hetarenopropionic acid and the predictability of the reaction product, while a negative aspect is the not always high yields, due to decomposition of the initial substances under the cyclization conditions. The method can be applied to the synthesis of cyclic ketones **20a-i** based both on furan, thiophene, and pyrrole and on their benzannelated derivatives **20j-n** (Schemes 1 and 2).

Scheme 1

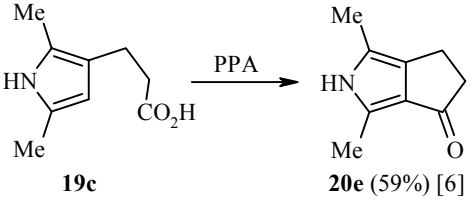
Synthesis of hetarenocyclopentanones



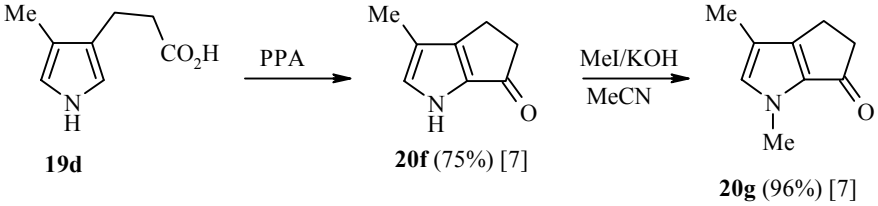
19a **20a** (34%) [4]



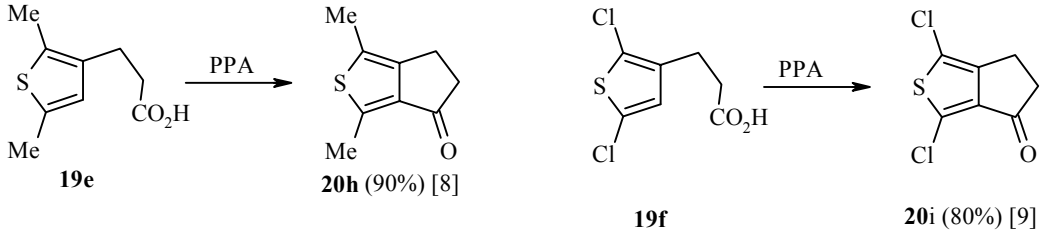
19b **20b** **20c** (51%) [17] **20d** (95%) [17]



19c **20e** (59%) [6]

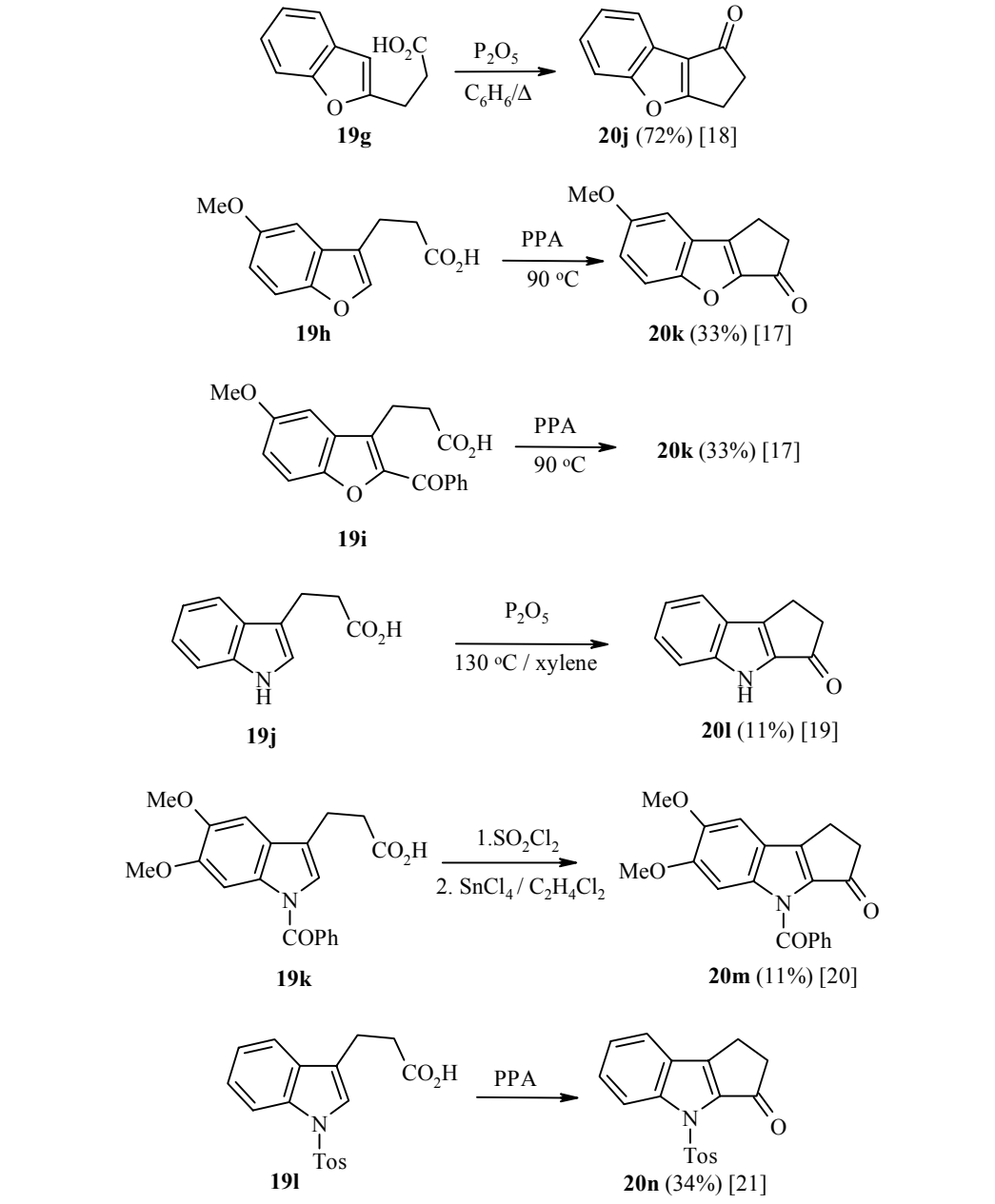


19d **20f** (75%) [7] **20g** (96%) [7]



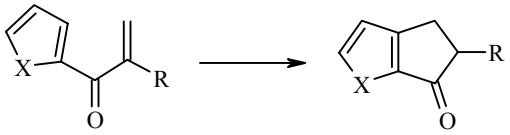
Scheme 2

Synthesis of benzohetarenocyclopentanones



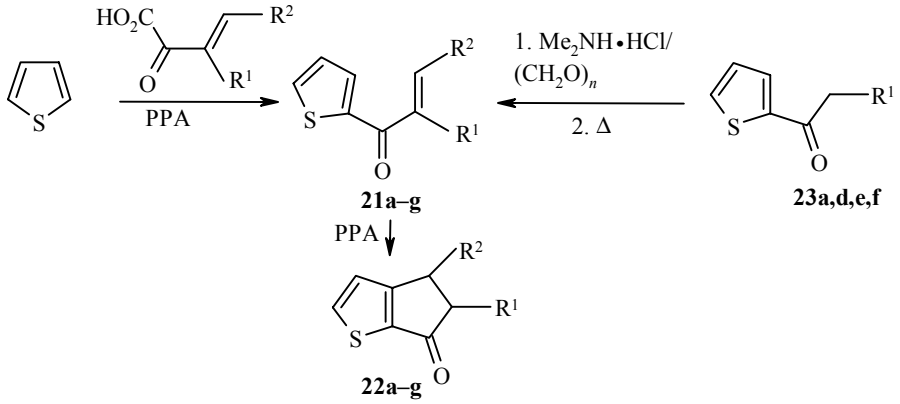
The yields of the desired ketones depend on the nature of the heterocycle. The highest yields were obtained in the case of thiophene and pyrrole. In the case of the benzannelated heterocycles the yields were average, and in the case of furans they were extremely low.

The cyclization of hetaryl vinyl ketones **21** to hetarenocyclopentanones **22**, which is a special case of the Nazarov reaction, has also been widely used in the synthesis of hetarenocyclopentanones.



21 **22**

By this method it is possible to obtain the desired compounds with fairly high yields, but the initial hetaryl vinyl ketones have been described little. They can be synthesized both by direct acylation of the heterocycle with substituted unsaturated acids and by decomposition of the Mannich bases obtained from hetaryl alkyl ketones [8]. In most cases the cyclization of thienyl vinyl ketone in PPA [8, 12] leads to the formation of cyclopentathiophenones with very good yields.

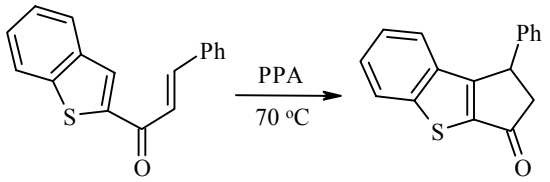


Cyclization of vinyl ketones in the benzothiophene and indole series also leads to the formation of cyclic ketones with yields varying from average to high.

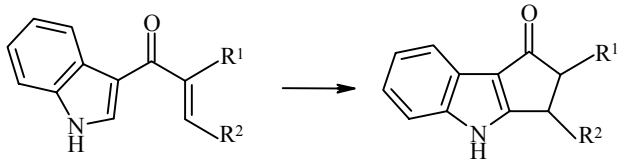
TABLE 2. Synthesis of Unsaturated Ketones and their Cyclization

Ketone				Yield, % (*)	Ketone				Yield, %
	Het	R^1	R^2			Het	R^1	R^2	
21a	2-Th	Me	H	79 (**23a**-95)	**22a**	2-Th	Me	H	84
21b	2-Th	H	Me	44	**22b**	2-Th	H	Me	68
21c	2-Th	H	Ph	81	**22c**	2-Th	H	Ph	3
21d	2-Th	Ph	H	79 (**23d**-87)	**22d**	2-Th	Ph	H	75
21e	2-Th	H	H	51 (**23e**-89)	**22e**	2-Th	H	H	0
21f	3-Th	Me	H	65 (**23f**-88)	**22f**	3-Th	Me	H	77
21g	3-Th	H	$(Me)_2$	61	**22g**	3-Th	H	$(Me)_2$	69

* The yield of the ketones **21** from 2-acylthiophenes **23** is given in parentheses.

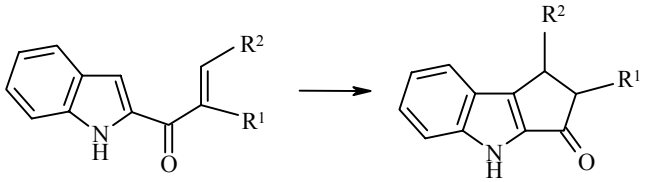


24 (36%) [19]



25a,**b**

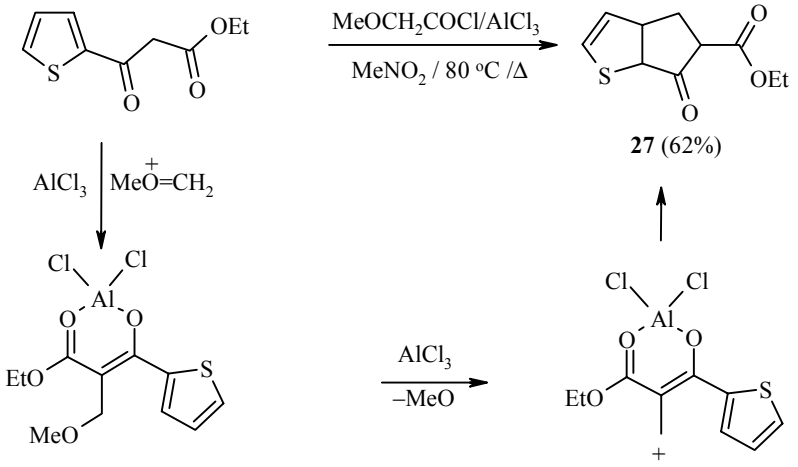
25 a $R^1 = R^2 =$ Me, (68%){20/80-*cis/trans*}, dioxane–H_2O, Δ; (15%){45/55-*cis/trans*}, $AlCl_3$ / NaCl / Δ; **b** $R^1–R^2 = –(CH_2)_4–$, (80%), dioxane–H_2O, Δ; [22]



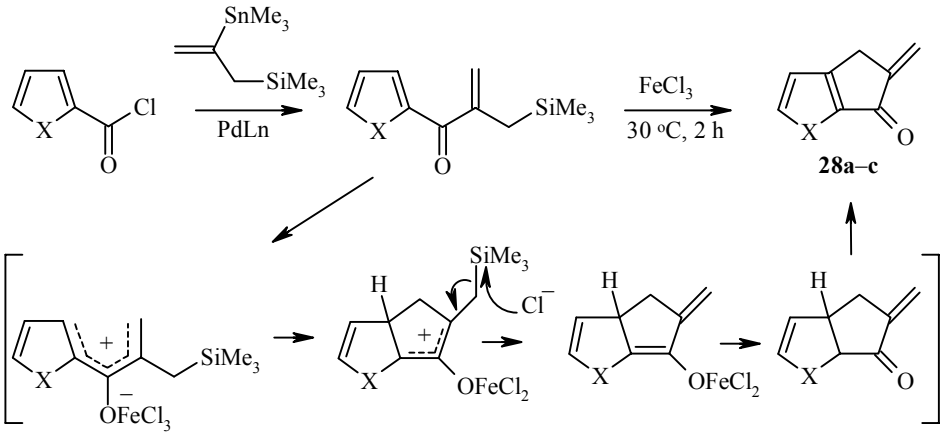
26a,**b**

26 a $R^1–R^2= –(CH_2)_4–$, (73%), dioxane / Δ;
b $R^1 = H$, $R^2 =$ Me, (73%), PPA / Δ [22]

A convenient method was developed for the synthesis of various 2-ethoxycarbonyl-1-indanones from readily obtainable β-dicarbonyl compounds by treatment with methoxyacetyl chloride in the presence of an excess of aluminum chloride [23]. The method made it possible to obtain ethyl 6-oxo-5,6-dihydro-4H-cyclopenta[*b*]thiophene-5-carboxylic acid (**27**), which was previously unobtainable by other methods. The β-dicarbonyl compound presumably undergoes alkylation by the methoxyacetyl chloride in the presence of the excess of aluminum chloride. The methoxy group is then eliminated, and cyclization occurs.

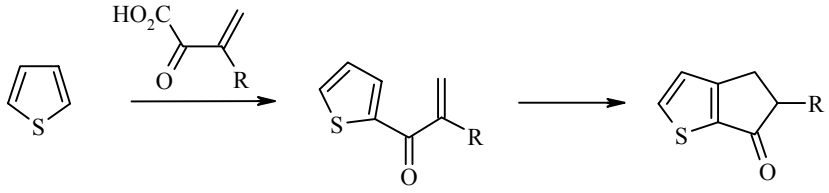


Modification of the Nazarov reaction using α-trimethylsilyl-substituted vinyl ketones was described in [24]. The cyclization of 2-thienyl and 2-furyl vinyl ketones and of 2-(N-methylpyrrolyl) vinyl ketone in the presence of a Lewis acid leads to the corresponding α-methylenecyclopentenones **28a-c**. The presence of trimethylsilyl groups is an essential condition for the occurrence of the reaction.



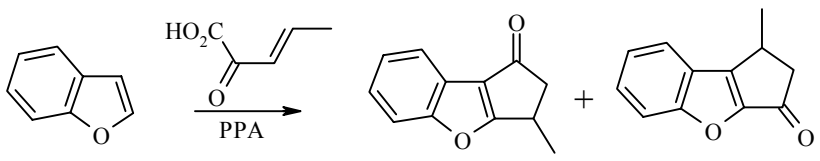
28 a X = O (52%); **b** X = NMe (48%); **c** X = S (65%)

Another general method for the synthesis of hetarenocyclopentanones is the single-stage addition of acrylic acids. Presumably, the reaction of the acrylic acids with the hetarenes results in the initial formation of an unsaturated ketone, which is then converted into the hetarenocyclopentanone.



In spite of the simplicity of the process, the method only makes it possible to obtain the desired compounds with acceptable yields in a limited number of cases. The low yields of the ketones can be explained by polymerization of the intermediately formed hetarenovinyl ketones and decomposition of the hetarenes under the reaction conditions.

The reaction of methacrylic acid with thiophene in polyphosphoric acid gave 5-methyl-4,5-dihydro-6H-cyclopenta[*b*]thiophen-6-one (**22a**) with a yield of 40% [8, 12]. The treatment of benzofuran with crotonic acid in polyphosphoric acid at 130°C led to the formation of 1-methyl-1,2-dihydro-3H-cyclopenta[*b*][1]furan-3-one (**29a**) together with a smaller amount of the isomeric 3-methyl-2,3-dihydro-1H-cyclopenta[*b*][1]furan-1-one (**29b**) [25].

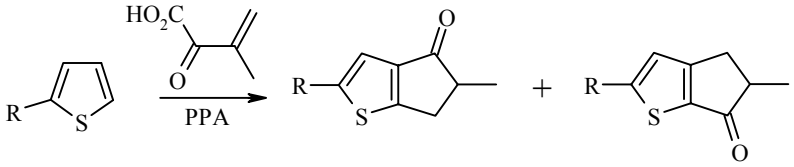


29a (34%) **29b**

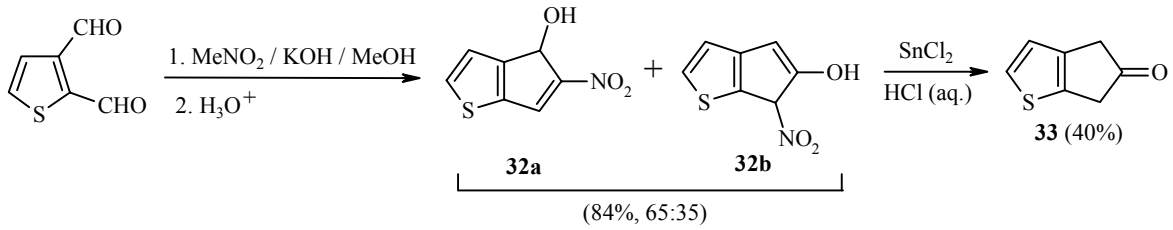
TABLE 3. The Yields of the Reaction Products and the Ratios of the Isomers

Compound	R	% of isomers		Yield, %
30a, 31a	H	99	1	7
30b, 31b	Me	70	30	15
30c, 31c	*t*-Bu	90	10	40
30d, 31d	Ph	60	40	15
30e, 31e	Cl	100	0	17
30f	Me	100	0	6

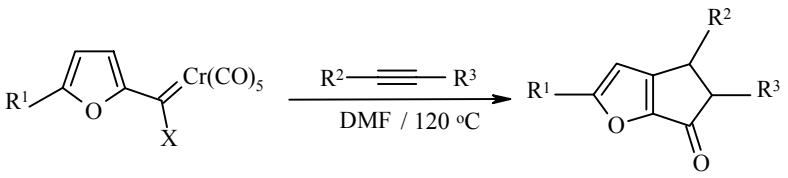
A logical continuation of research on the intramolecular cyclization of vinyl ketones of the thiophene series is investigation of the reaction of 2-substituted thiophenes with methacrylic acid in polyphosphoric acid [26]. The yields and the ratios of the products of the reaction of 2-substituted thiophenes with methacrylic acid in polyphosphoric acid are given in Table 3.



There are a number of special methods for the synthesis of hetarenocyclopentanones. Thus, for example, a convenient method has been described for the synthesis of cyclopentathiophen-5-one, which is a heteroanalog of 2-indanone, by the reaction of 2,3-diformylthiophene with nitromethane in a methanol solution of potassium hydroxide [27]. This method makes it possible to synthesize 4,6-dihydro-5H-cyclopenta[*b*]thiophen-5-one (**33**), which is difficult to obtain by other methods.



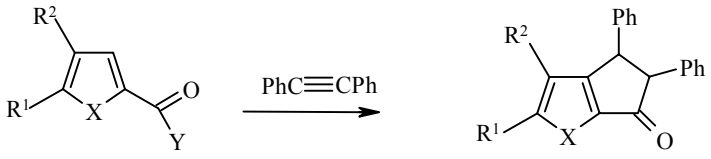
It was proposed to use the cycloaddition of acetylenes to furanchromium carbene complexes for the synthesis of cyclopentanones [28]. The yield of the oxacyclopentanones was fairly high, but widespread use of the method was prevented by the poor availability of the initial carbonyl complexes of chromium.



X = OMe, R^1 = H;
X = OMe, R^1 = Me;
X = N-morpholyl, R^1 = H

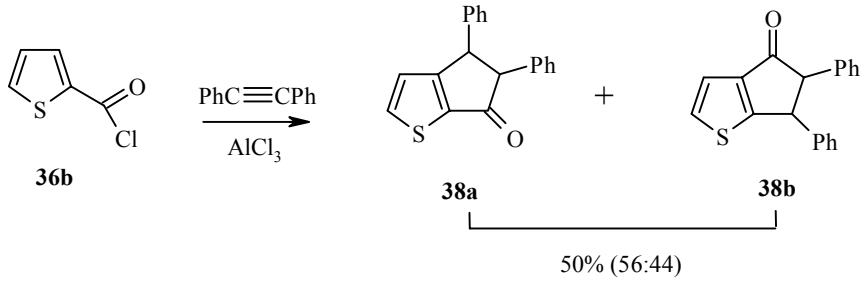
34a–f R^1 = Me, H; R^2 = Ph, *n*-Bu, $CH_2CH{=}CH_2$, $(CH_2)_2C{=}CH_2$; R^3 = Ph, *n*-Bu, *t*-Bu, (10–37%)

A curious method based on tolane and iron(II) heteroylcyclopentadienylcarbonyl was described for the synthesis of diphenylcyclopentanes annelated with furan, benzofuran, and thiophene [29, 30].



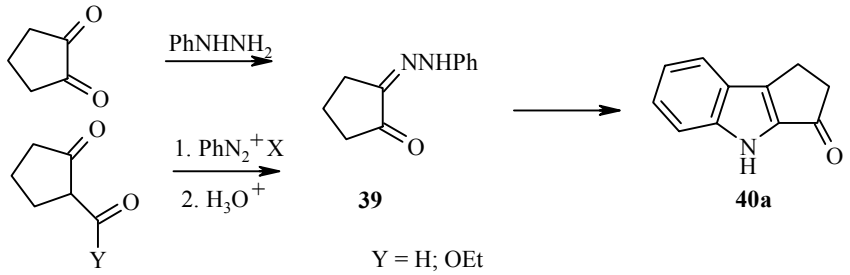
Y = σ-CpFe(CO)$_2$;
35 a X = O, R^1 = Me, R^2 = H; **b** X = O, R^1–R^2 = (–CH=CH–CH=CH–); **36 a** X = S, R^1 = R^2 = H
37 a X = O (30%); **b** X = O (48%); **38 a** X = S (52%)

It was established that the reaction of thiophenecarbonyl chloride with tolane in the presence of aluminum chloride led to the formation of diphenylcyclopenta[*b*]thiophenones [30]. A mixture of 5,6-diphenyl-4H-cyclopenta[*b*]thiophen-4-one and 4,5-diphenyl-6H-cyclopenta[*b*]thiophen-6-one was formed.

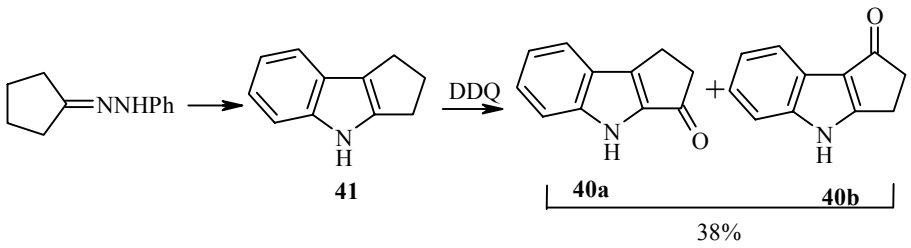


In the authors' opinion the reaction mechanism includes the addition of tolane at the activated carbonyl group followed by attack on the heterocycle by the vinyl carbocation that forms. The formation of a mixture of compounds **38a** and **38b** is explained by the possibility of rearrangement of the cation.

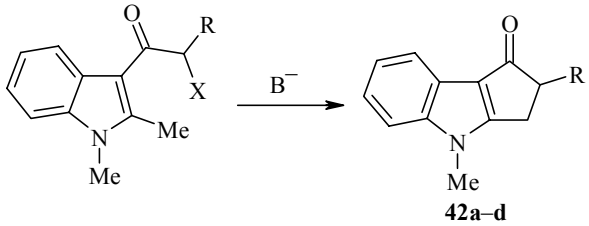
A special but very effective method for the synthesis of indolocyclopentanone **40a** is Fischer indolization of 1,2-cyclopentanedione arylhydrazone **39**, which can be produced both directly from 1,2-cyclopentanedione and the arylhydrazine and as a result of rearrangement of the product from the addition of a diazonium salt to 2-formyl-1-cyclopentanone [31] or 2-ethoxycarbonyl-1-cyclopentanone [32].



An alternative approach to the synthesis of the ketones involves the oxidation of 1,2,3,4-tetrahydrocyclopenta[*b*]indole (**41**), formed by the Fischer reaction from cyclopentanone phenylhydrazone, with 2,3-dichloro-5,6-dicyanoquinone (DDQ) [33]. The reaction gives a mixture of isomeric ketones (6.5:1) with the preferential formation of **40a**.



During study of the rearrangements of 3-(α-halogenoacyl)indoles catalyzed by bases (hydroxides, hydrides, Grignard reagents) it was found [34] that in the case of N-methyl-2-methyl-3-(α-halogenoacyl)indoles the 2-substituted 3,4-dihydrocyclopenta[*b*]indol-1(2H)-ones **42a-d** are formed as a result of the rearrangement.

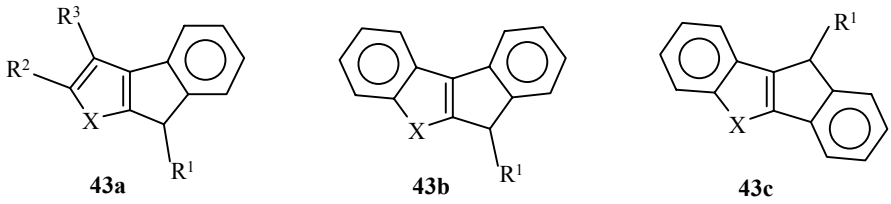


42a–d

42 a R = H, X = Br (4**%)**; **b** R = Me, X = Br (54%);
c R = Et, X = Br (91%); **d** R = Ph, X = Br (80%)

2. SYNTHESIS OF INDENOHETEROCYCLES AND THEIR BENZANNELATED ANALOGS

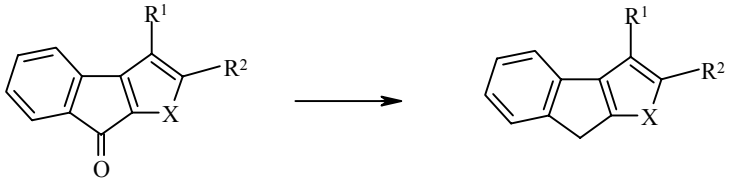
Compounds of structural types **43a-c** (X = S, O, NR), which can be represented as heteroanalogs of fluorene, are usually obtained from the corresponding cyclic ketones. The synthesis of the thia and aza derivatives has been widely investigated, whereas the synthesis has been developed very poorly for the oxa derivatives.



43a **43b** **43c**

It is possible to identify several ways of producing the desired compounds **43a-c**: Reduction of cyclic ketones (the required cyclic ketones are usually obtained by intramolecular cyclization of the respective carboxylic acids and their derivatives); rearrangement of dihetarylarylcarbinols in an acidic medium; specific methods for the synthesis of hetarenoindenes; specific methods for the synthesis of indenopyrroles and indenoindoles.

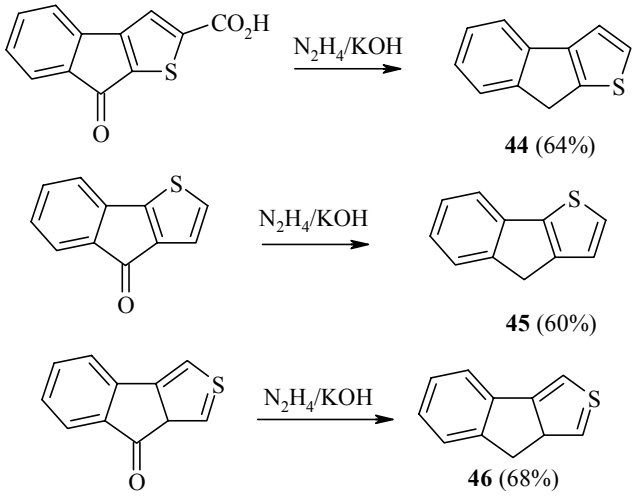
2.1. Synthesis of Hetarenoindenes by Reduction of Cyclic Ketones



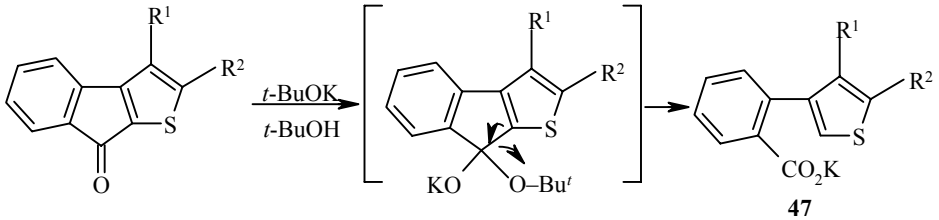
The principal ways of transforming hetarenoindenones into hetarenoindenes involve either reduction of cyclic ketones by the Kishner–Wolff method with hydrazine in the presence of potassium hydroxide or with $LiAlH_4/AlCl_3$ in ether.

In most cases Kishner–Wolff reduction is fairly effective. The small yields obtained in individual cases can be explained by opening of the ketone ring under the reaction conditions.

Indenothiophenones were reduced with good yields by hydrazine in the Kishner–Wolff method [35]. In the case of 8-oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylic acid reduction with simultaneous decarboxylation made it possible to obtain 8H-indeno[2,1-*b*]thiophene (**44**) with a yield of 64%. However, when decarboxylation was conducted first and followed by reduction, the yield of compound **44** amounted to only 37%, and if an excess of hydrazine was used the yield was reduced to 10%.



The action of a strong base (potassium *tert*-butoxide in *tert*-butanol, ether, or dioxane) led to cleavage of the C–(C=O) bond in the thia analogs of fluorenone at room temperature within a short time [36]. The proposed mechanism includes attack by the *tert*-butoxide anion at the carbonyl group of the ketone, cleavage of the bond with the thiophene ring, and subsequent elimination of the *tert*-butoxide anion.



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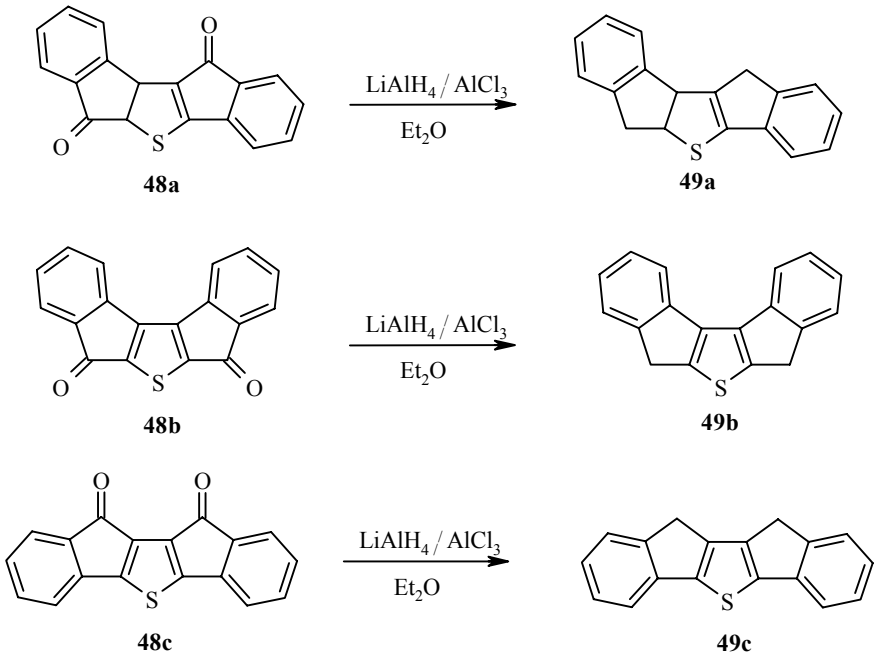
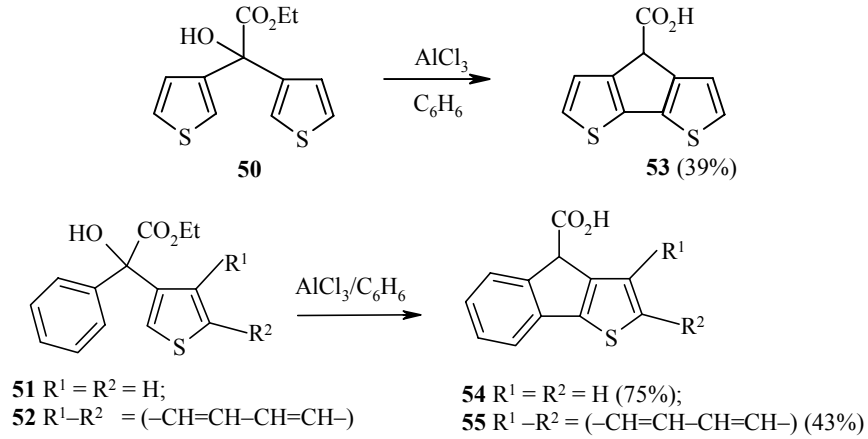
It is extremely likely that a side process takes place during Kishner–Wolff reduction, and this reduces the yield of the reduction product.

Reduction of the diindenothiophenediones **48a-c** with a $LiAlH_4/AlCl_3$ mixture in ether leads to the corresponding diindenothiophenes **49a-c** with yields of 70% [37].

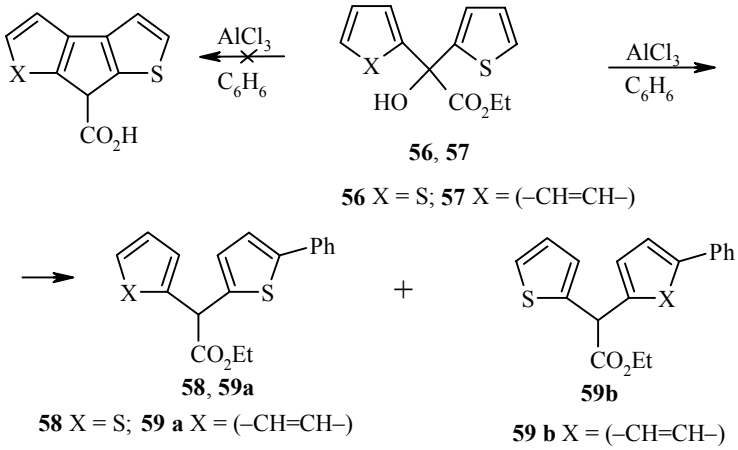


2.2. Rearrangement of Dihetarenoarylcarbinols in an Acidic Medium

The action of an excess of $AlCl_3$ in benzene on ethyl esters of 2,2-di(3-thienyl)glycolic (**50**), 2-phenyl-2-(3-thienyl)glycolic (**51**), and 2-(3-benzothienyl)-2-phenylglycolic (**52**) acids leads to intramolecular cyclization with the formation of polycyclic compounds **53-55** [38].



At the same time the derivatives of 2-aryl-2-(2-thienyl)glycolic acids **56** and **57** do not form polycyclic compounds under the same conditions but only the corresponding phenylation products **58** and **59a**,**b**.



56, **57**

56 X = S; **57** X = (–CH=CH–)

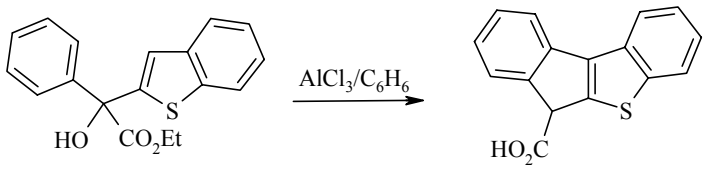
58, **59a**

58 X = S; **59 a** X = (–CH=CH–)

59b

59 b X = (–CH=CH–)

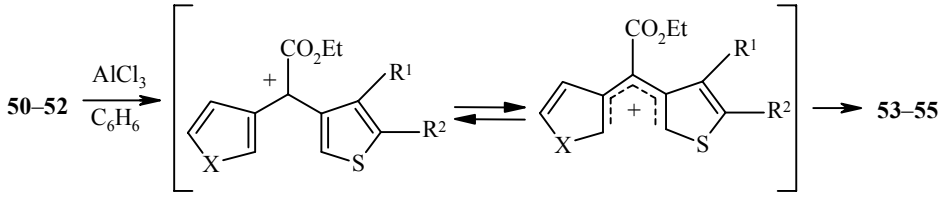
The exception is ethyl ester of 2-phenyl-2-(2-benzothienyl)glycolic acid (**60**), which forms 6H-indeno[2,1-*b*][1]benzothiophene-6-carboxylic acid (**61**) with a fairly high yield. Traces of phenylated compounds were not found, but replacement of the solvent (from benzene to carbon disulfide) led to a threefold increase of the yield.



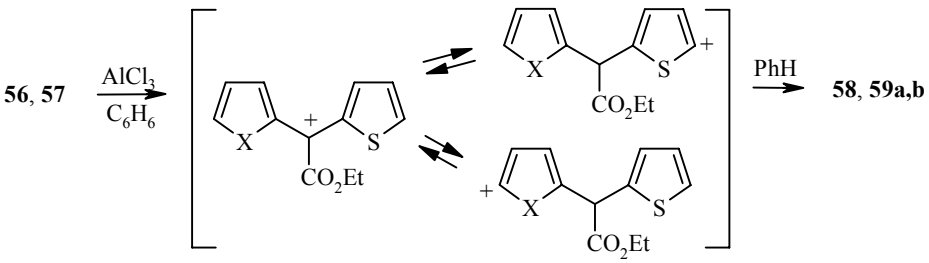
60

61 (21%); (67% $–CS_2$)

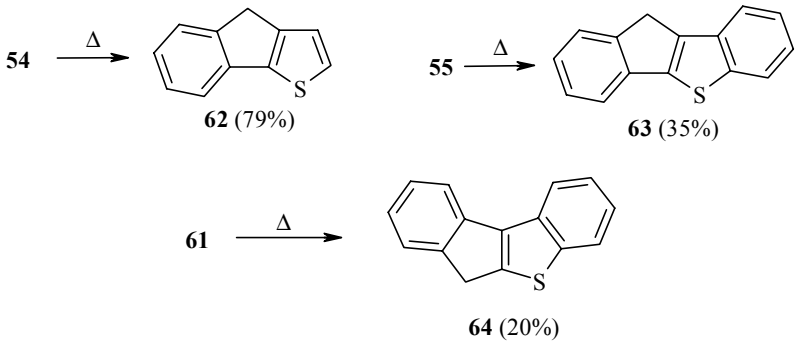
The authors proposed a mechanism for the formation of the ring similar to the Nazarov reaction with involving cyclization of the carbocation formed during the reaction of the glycolic acid with the excess of aluminum chloride.



The formation of compounds containing phenyl groups when an excess of aluminum chloride in benzene is used for the esters of acids **56** and **57** may be due to electrophilic attack by the intermediately formed cation on the benzene used as solvent.

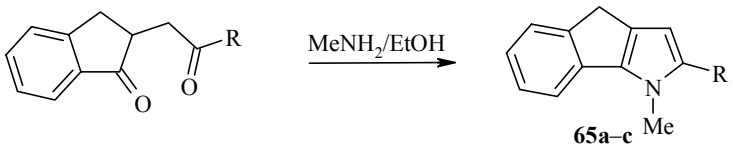


Carboxylic acids of the indenothiophene and indenobenzothiophene series are decarboxylated with yields both low (in the case of benzothiophenoindenes) and high (in the case of indenothiophene).



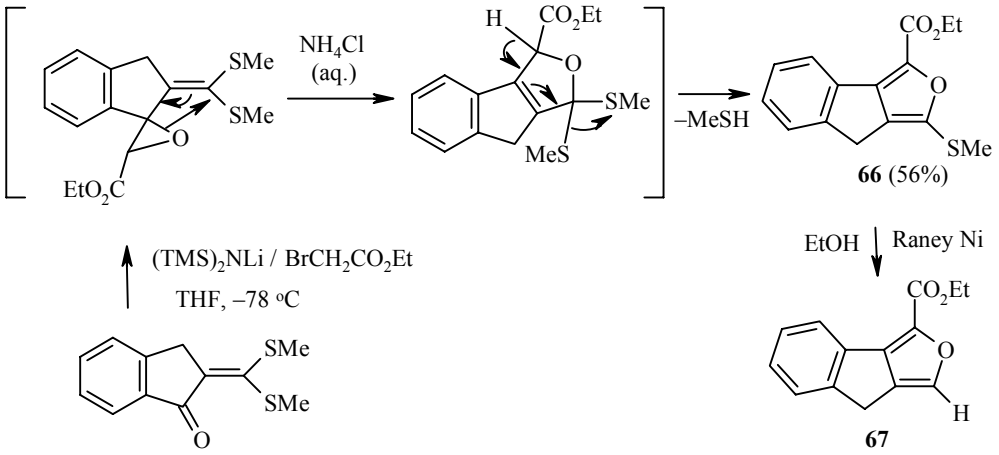
2.3. Specific Methods for the Synthesis of Hetarenoindenes

The 1,4-dicarbonyl derivatives of 1-indanone and 2-indanone, which can easily be transformed by the Paal–Knorr reaction into the respective dihydroindenopyrroles, dihydroindenothiophenes, and dihydroindenofurans, are widely used. The main disadvantages of the method are the poor availability of the initial 1,4-dicarbonyl compounds and the not very high yields.

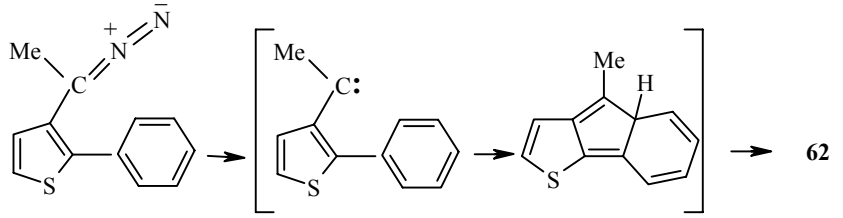


65 a R = Et (36%); **b** R = Pr (31%); **c** R = Ph (22%)

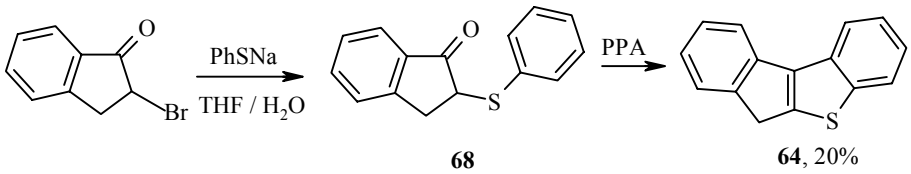
The Darzens reaction for derivatives of α-oxo ketones has been used as a suitable method for the synthesis of indeno[*c*]furans [40].



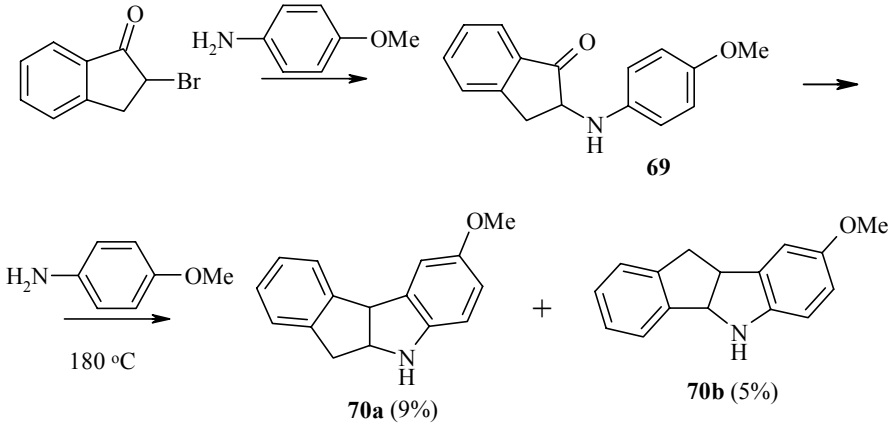
Phenyldiazoalkylthiophenes, generated from the sodium salts of tosylhydrazone, undergo electrocyclic rearrangement, and only in the case of 3-diazoalkyl-2-phenylthiophene does this lead to the formation of the tricycle **62** with a yield of 92%. In other cases either thiophene dimers are formed, or the thiophene ring is opened [41].



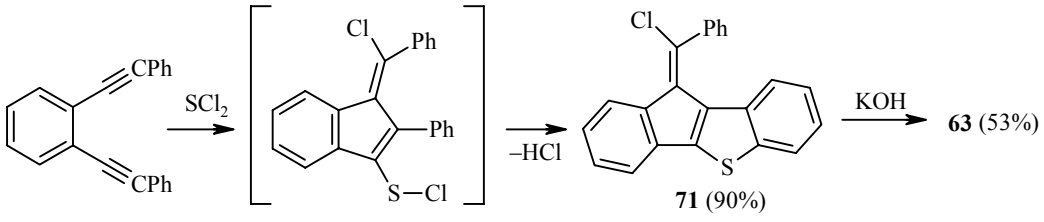
Intramolecular cyclization of 2-phenylthio-1-indanone (**68**) in polyphosphoric acid [38] gave 6H-indeno[2,1-*b*]benzothiophene (**64**). This is an alternative to the intramolecular cyclization of ethyl phenyl(benzothienyl)glycolate in benzene and carbon disulfide in the presence of an excess of aluminum chloride followed by decarboxylation [38].



A similar procedure with cyclization of α-amino ketones leading to the formation of indoles (the Bischler reaction) was used for the synthesis of indenoindoles [42]. For example, the reaction of *p*-anisidine with 2-bromo-1-indanone led to the formation of a mixture of isomeric indenoindoles **70a**,**b** with an overall yield of 14%.

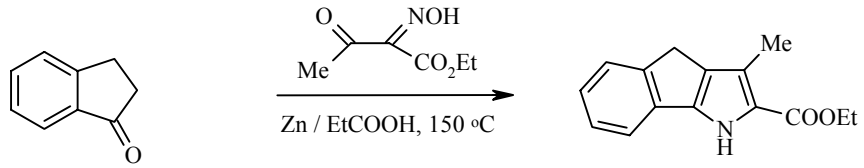


The isomeric 10H-indeno[1,2-*b*]benzothiophene (**63**) was obtained as a result of alkaline hydrolysis of the phenylchlorofulvene of 10H-indeno[1,2-*b*]benzothiophene (**71**) [43], formed during the electrophilic addition of SCl_2 to 1,2-bis(phenylethynyl)benzene.

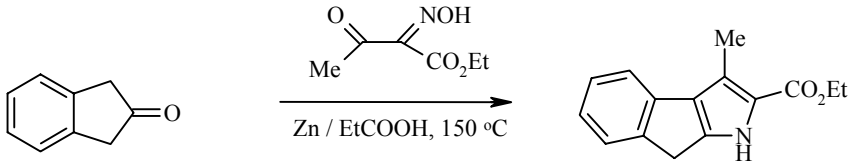


The synthesis of indenopyrrole and indenoindoles is specific in nature, since the usual methods for the production of such compounds are reactions well known in the synthesis of pyrrole and indoles.

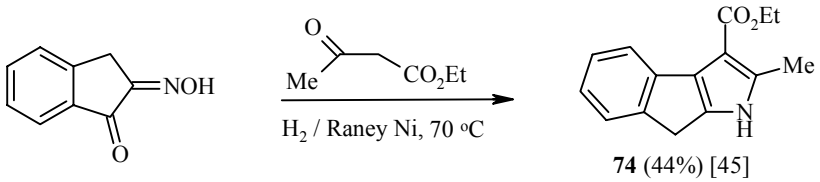
The reaction of derivatives of 1-indanone and 2-indanone with α-aminocarbonyl compounds is widely used in the synthesis of indenopyrroles.



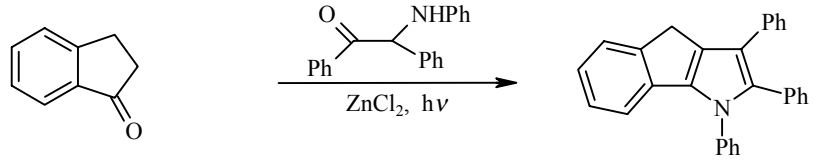
72 (22%) [44]



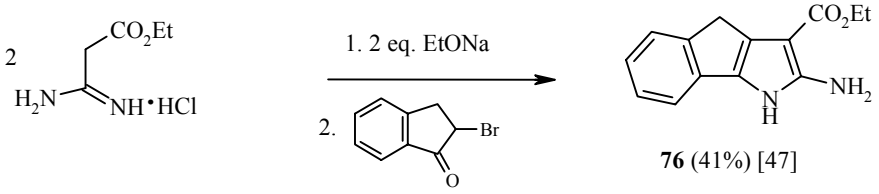
73 (34%) [44]



74 (44%) [45]

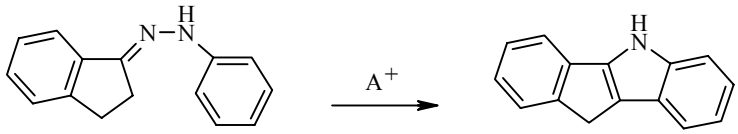


75, (5%) [46]



76 (41%) [47]

The most general and convenient method for the production of indenoindoles is the acid-catalyzed rearrangement of the arylhydrazones of indanones, known as the Fischer reaction.



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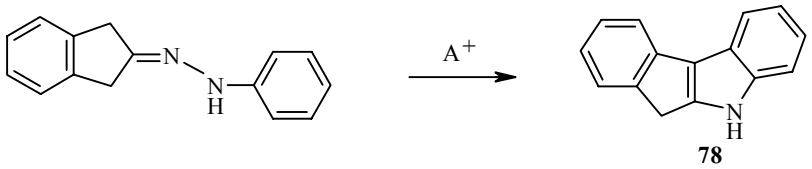
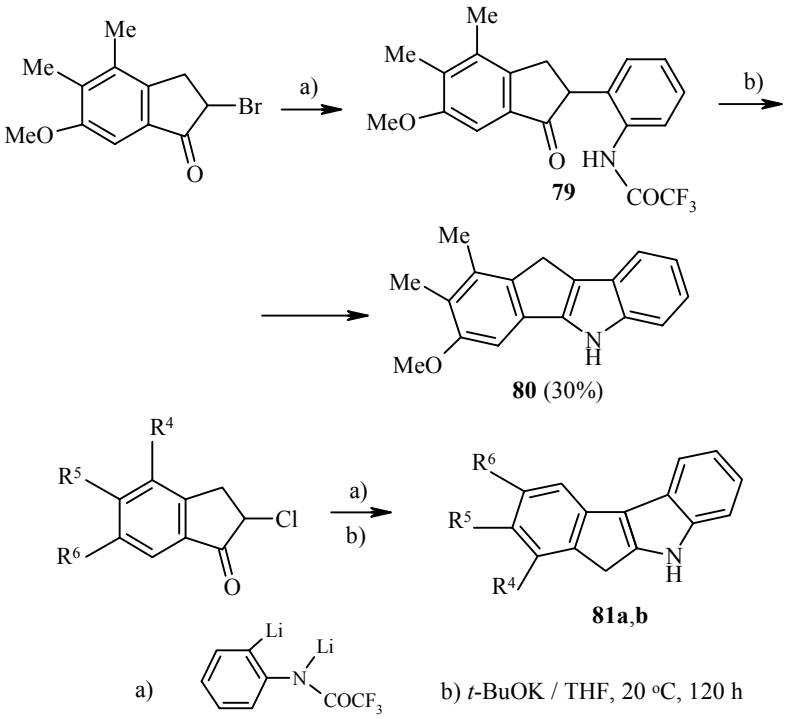


78

The method was used to obtain a series of indenoindoles containing various substituents both in the indole and in the indene fragment [48-62]. The yields of the compounds amounted to 9-95%. The only limitation of the method is the synthetic availability of the indanones or hydrazines.

The Wender reaction was used for the synthesis of certain indenoindoles containing Me and MeO groups in the indene fragment [42, 63], and the reaction is conducted both in one stage [63] and with the isolation of the intermediate product trifluoro-N-[2-(1-oxo-2-indanyl)phenyl]acetamide [50]. The direction of the process depends on the nature of the halogen, which makes it possible to obtain the isomeric indenoindoles.



79

80 (30%)

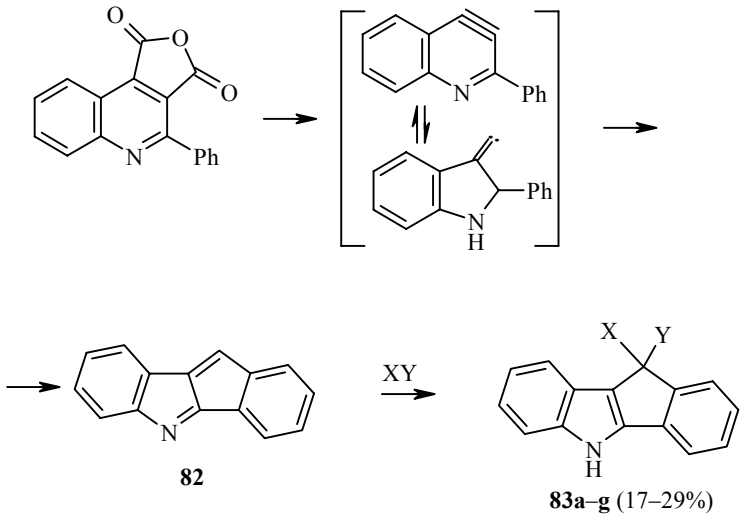
81a,**b**

a) b) *t*-BuOK / THF, 20 °C, 120 h

81 a $R^4 = R^5 = R^6 = H$, 46%; **b** $R^4 = R^6 = H$, $R^5 = OMe$, 51%

For compound **79** it should be noted that a side product was the indane intermediate (16%), while in the case of 2-chloro-1-indanone it was found that alcohol intermediate products were not formed. Unsubstituted 2-chloro-1-indanone was enolized by the action of a base, and the desired compound could only be obtained as a result of the addition of $CeCl_3$ to the mixture. It is interesting that when cerium(III) chloride was used for the methoxy-substituted chloroindane the yield of the respective indenoindole **81** was reduced from 51 to 30% [42].

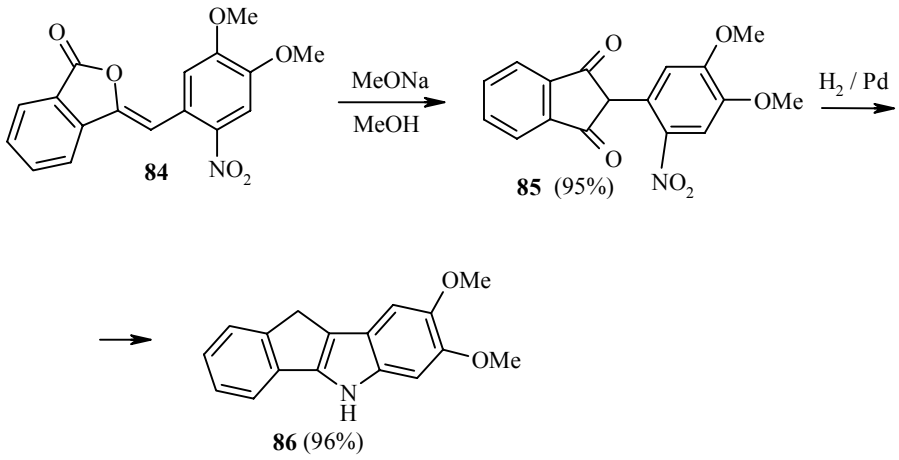
A fairly unusual method for the synthesis of a series of derivatives of dihydroindeno[1,2-*b*]indole involves the action of various nucleophilic reagents on indeno[1,2-*b*]indole, which is formed from 2-phenylquinoline-3,4-carboxylic anhydride during vacuum pyrolysis at 800°C (0.06 mm Hg) [64]. This method is of some value for studying the chemistry of indeno[1,2-*b*]indole, which it has not yet been possible to obtain by other methods.



82 **83a–g** (17–29%)

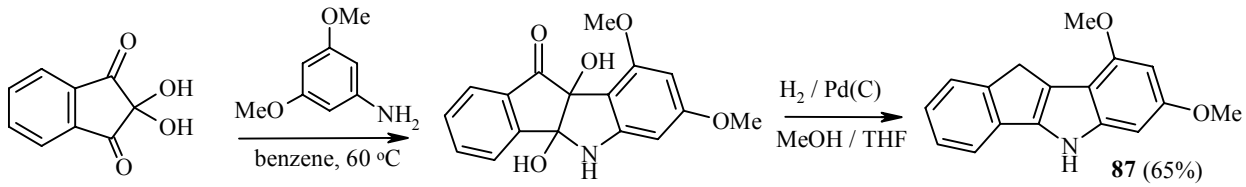
XY = $LiAlH_4$; $HNEt_2$; PhLi; MeONa; MeMgI; $NaCH(CO_2Me)_2$; $NaCH_2NO_2$

An extremely effective method for the synthesis of 7,8-dimethoxy-5,10-dihydroindeno[1,2-*b*]indole (**86**) involves the action of sodium methoxide in methanol on the nitrolactone **84**, which is produced by heating a mixture of phthalic anhydride, 3,4-dimethoxy-2-nitrophenylacetic acid, and sodium acetate at 240°C, and then catalytic hydrogenation of the obtained indandione **85** [65].



84 **85** (95%) **86** (96%)

During the synthesis of 7,9-dimethoxy-5,10-dihydroindeno[1,2-*b*]indole (**87**) by the action of ninhydrin on 3,5-dimethoxyaniline followed by hydrogenation of the intermediately formed compound electrophilic substitution occurs at the *ortho* position to the amino group of the 3,6-dimethoxyaniline instead of nucleophilic attack by the amino group at the ninhydrin [66].



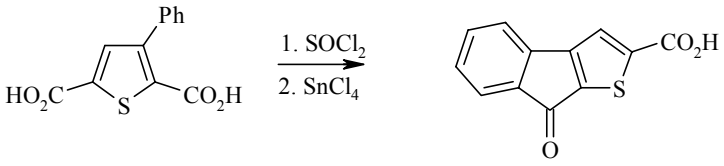
87 (65%)

There are two main methods for the production of N-substituted dihydroindenoindoles. The first is based on the use of N-substituted arylhydrazones in the Fischer reaction. However, on account of the poor availability of the starting compounds the real application of this approach is the production of N-phenyldihydroindenoindoles. The second method involves direct introduction of the substituent into unsubstituted dihydroindenoindole. This method is suitable for N-alkylation [59] and N-acylation [57, 67-69].

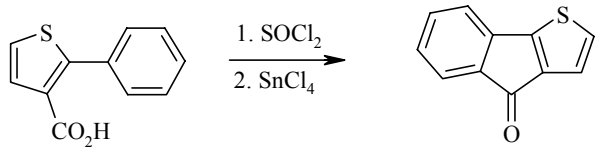
2.4. Synthesis of Indenobenzohetarenoketones

As in the case of hetarenopentalenes, the main synthetic precursors for hetarenoindenes and benzoarenoindenes are cyclic ketones. Interest in structures of this type is due to the fact that many of them, and particularly the oxa and aza derivatives, have biological activity.

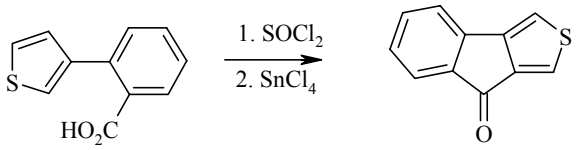
The main method for the synthesis of cyclic ketones is the intramolecular cyclization of carboxylic acids and their derivatives under various conditions.



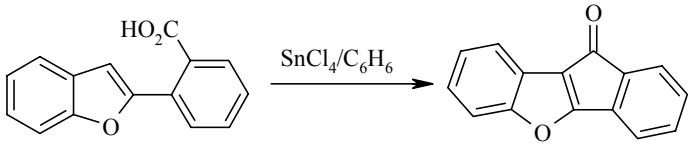
88 (59%) [35]



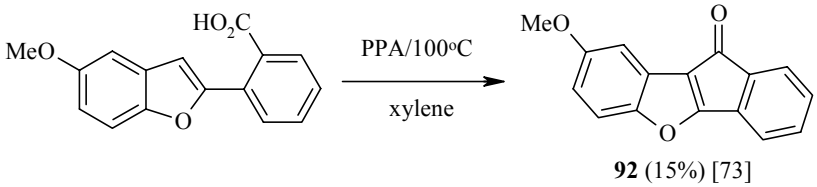
89 (82–91%) [70]



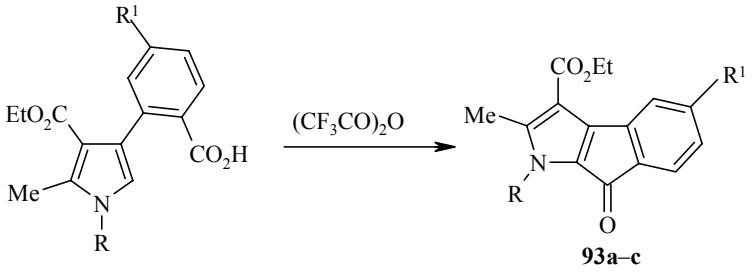
90 (78%) [71, 72]



91 (36%) [73]

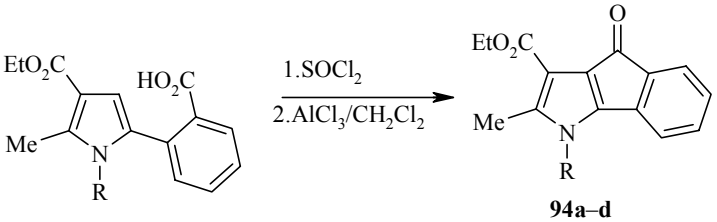


92 (15%) [73]



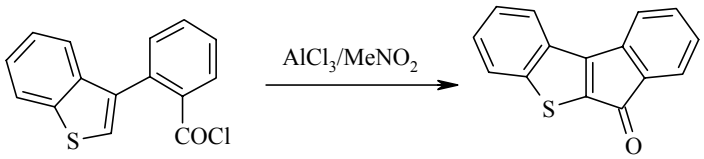
93a–c

93a R = Me, R^1 = Br (89%); **b** R = CH_2Ph, R^1 = H (84%);
c R = CH_2COPh, R^1 = H (71%) [74]

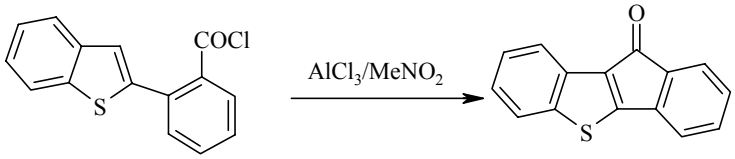


94a–d

94a R = Me (61%); **b** R = Ph (84%); **c** R = 4-MeC_6H_4 (72%);
d R = CH_2Ph (71%) [75]

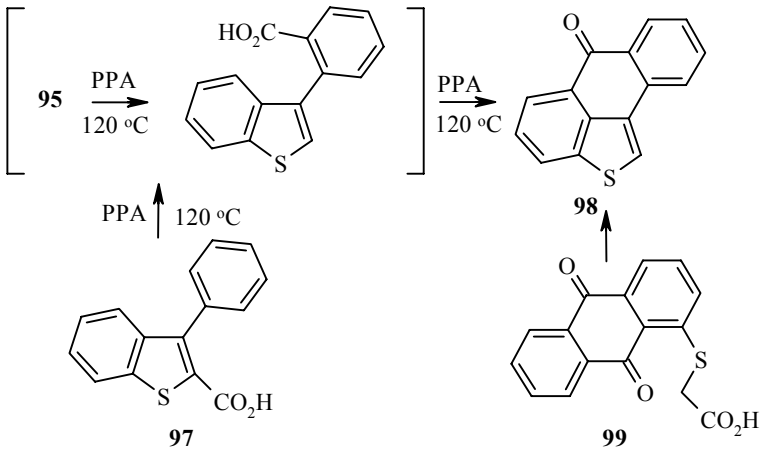


95 (80%) [76]

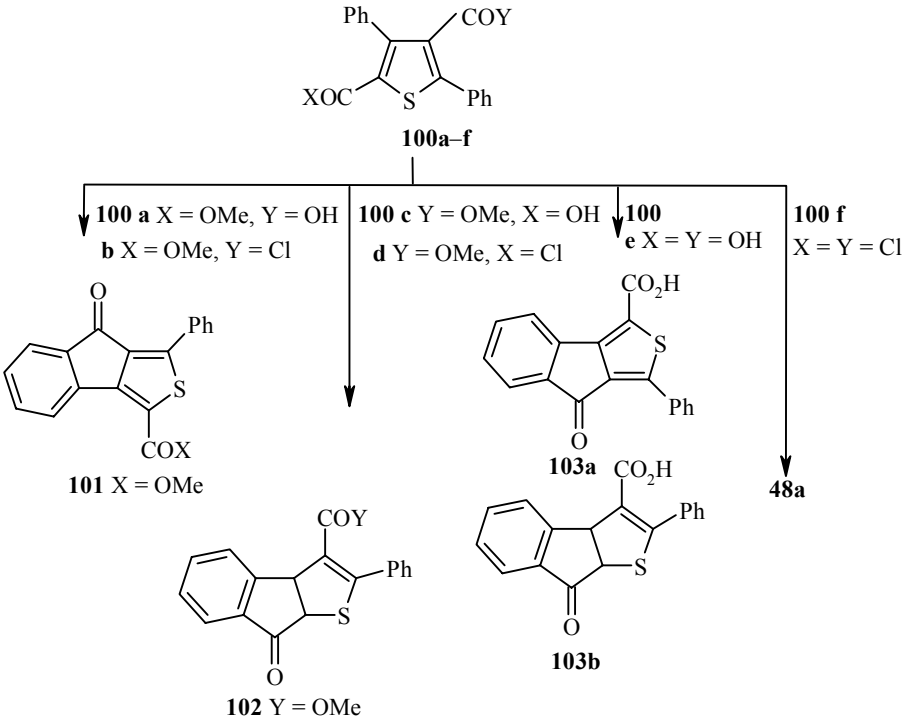


96 (70%) [77]

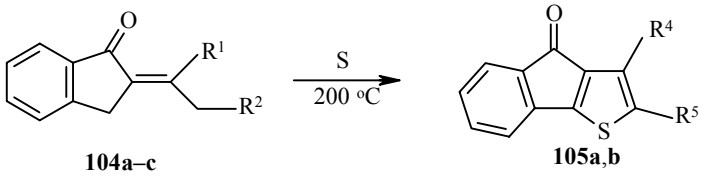
It was shown that compound **98**, which differs from the expected **95**, was formed during an attempt at the direct cyclization of 3-phenylbenzo[*b*]thiophene-2-carboxylic acid in polyphosphoric acid. The structure of the obtained compound was confirmed by an alternative synthesis from the quinone **99** [78]. A possible mechanism of formation is presented below.



The cyclization of 3,5-diphenyl-2,4-thiophenedicarboxylic acid and its derivatives in polyphosphoric acid gives fairly high yields (~70%), and the structure of the cyclization product depends on which derivative of the acid enters into the reaction [79].

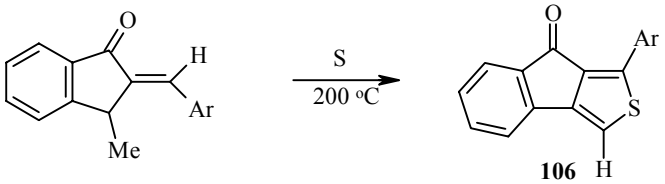


Apart from the intramolecular cyclization of carboxylic acids or their derivatives there are a series of other special methods for the synthesis of cyclic ketones. Thus, for example, sulfur adds to the alkyl- and arylmethylene derivatives of 1-indanone at elevated temperatures (~200°C) with the formation of substituted indenothiophenones [80].



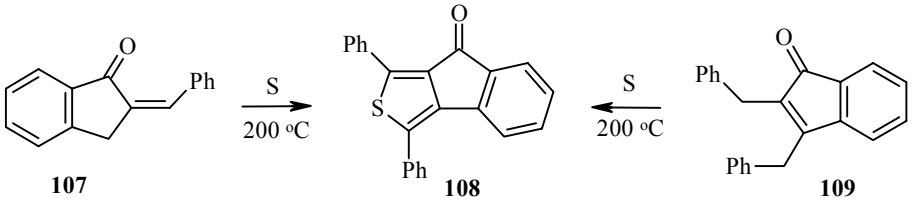
104 a R^1 = Me, R^2 = H; **b** R^1 = H, R^2 = Me; **c** R^1 = Et, R^2 = H.

105 a R^4 = R^5 = H, 35%; **b** R^4 = R^5 = Me, 17%



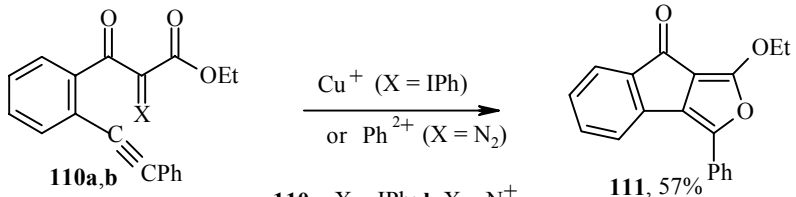
106 (Ar – substituted Ph, Th), 20–36 %

The action of sulfur on 2-benzylidene-1-indanone (**107**) leads to the formation of 1,3-diphenylindeno[1,2-*c*]thiophen-4-one (**108**) with an extremely small yield (<5%) due, as the authors suppose, to probable intermolecular transfer of the benzylidene fragment during the reaction and subsequent formation of the thiophene ring. The structure of the compound formed was confirmed by an alternative synthesis from 2,3-dibenzylinden-1-one (**109**).



107 **108** **109**

In the course of an investigation of certain diazo and iodonium derivatives of 2-(phenylethynyl)benzoylacetic ester **110a**,**b** it was unexpectedly found that catalysis of the decomposition of the iodonium ylide **110a** by copper(II) salts led to the formation of 1-ethoxy-3-phenylindeno[1,2-*c*]furan-8-one (**111**). The same compound was obtained as a result of the decomposition of the α-diazo ketone **110b** catalyzed by rhodium(II) salts [81].



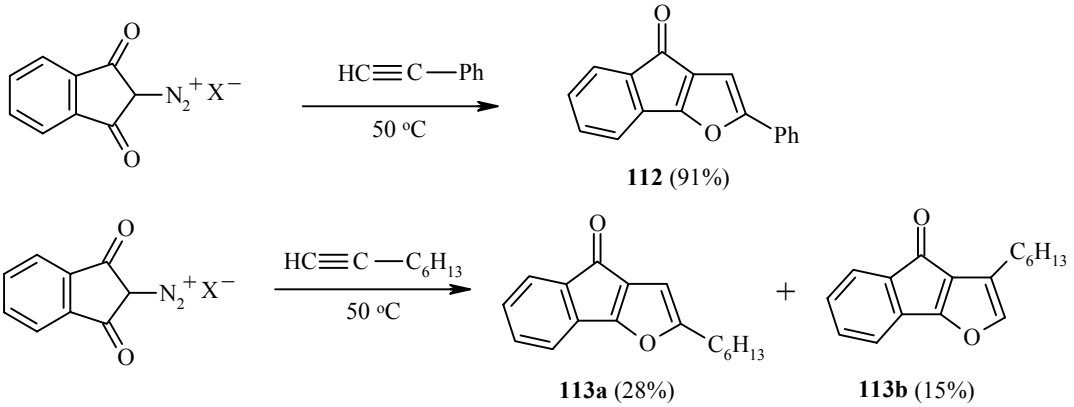
110a,**b**

110 a X = IPh; **b** X = N_2^+

111, 57%

The authors assume that the motivating force of the reaction in the case of catalysis by copper(II) salts is the formation of a carbene and its subsequent addition at the acetylene bond. In the case of decomposition of the α-diazo ketone catalyzed by rhodium(II) salts a rhodium carbenoid is initially formed with the loss of nitrogen. The addition of this carbenoid to the acetylenic π-system results in the formation of a vinylic carbenoid and the subsequent formation of a carbonyl ylide. Aromatization of the ring that forms leads to 3-phenyl-1-ethoxyindeno[1,2-*c*]furan-8-one.

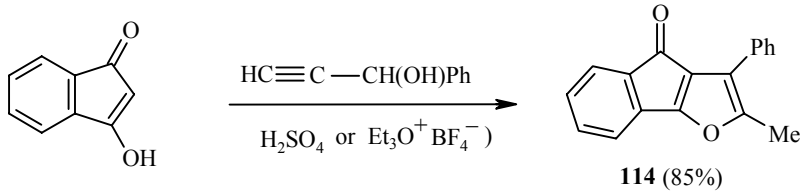
The decomposition of 2-diazo-1,3-indanedione in phenylacetylene at 50°C leads to the formation of 2-phenyl-4H-indeno[1,2-*b*]furan (**112**) [82]. 1,3-Dipolar addition of the carbene formed as a result of the decomposition of 2-diazo-1,3-indanedione to phenylacetylene is regioselective and results the formation of a compound containing hydrogen at position 3 of the furan ring. However, in the case of other acetylenes a mixture of the two possible stereoisomers is observed. For example, in the case of 1-octyne a mixture of 2-hexyl-4H-indeno[1,2-*b*]furan (**113a**) and 3-hexyl-4H-indeno[1,2-*b*]furan (**113b**) was obtained.



112 (91%)

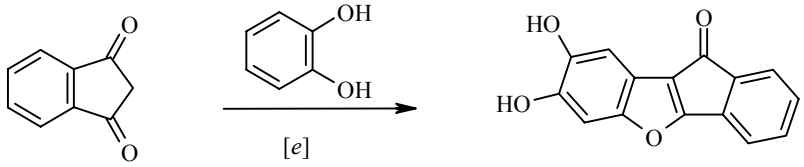
113a (28%) **113b** (15%)

Under the conditions of acid catalysis (sulfuric acid or boron trifluoride etherate) the addition of 3-phenylpropargyl alcohol to 1,3-indanedione led to the synthesis of 2-methyl-3-phenyl-4H-indeno[1,2-*b*]furan-4-one (**114**) [83]. The propargyl cation formed by the action of the acid adds at position 2 of 1,3-indanedione, and attack by the carbonyl group at the multiple bond leads to the formation of indenofuranone.



114 (85%)

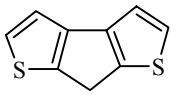
An elegant method for the synthesis of 7,8-dihydroindeno[1,2-*b*]benzo[*b*]furan-10-one (**115**) from pyrocatechol and 1,3-indanedione in an electrochemical cell was described in [84].



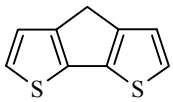
115 (96%)

3. SYNTHESIS OF DITHIENOCYCLOPENTADIENES

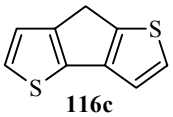
Of the dihetarenocyclopentadienes only dithiophenocyclopentadienes (denoted subsequently as Th_2Cp) have been described in the literature. These compounds are the diheteroanalogs of fluorene and can exist in the form of six isomers differing in the position of the heteroatom in relation to the allylic position of the cyclopentadiene. The synthesis of all six isomeric unsubstituted dithienocyclopentadienes **116a-f** has been described [85-87].



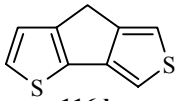
116a



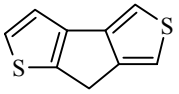
116b



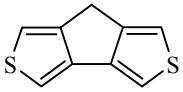
116c



116d



116e

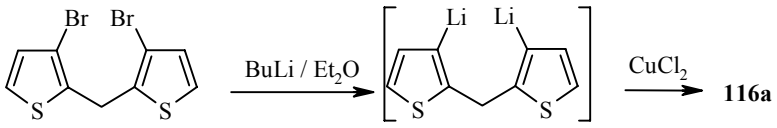


116f

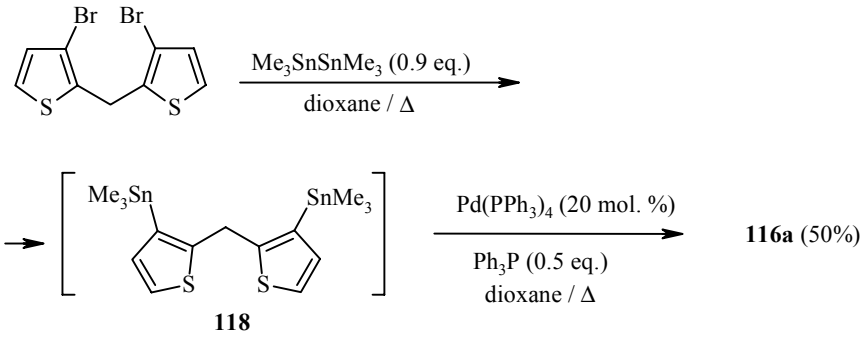
The compounds are stable and convenient to handle. However, the inadequate study of Th_2Cp can be explained by the fact that their synthesis is extremely laborious, consists of several stages, and gives extremely low yields.

To the present day only two methods are known for the synthesis of compounds of this structural type. (Since the methods were applied to all the isomeric dithienylmethanes only the reactions for one isomer are given in the schemes.) The first method involves transformation of the respective bis(bromothienyl)methanes into the corresponding organodimetallic derivatives followed by their oxidative cyclization.

Thus, the action of butyllithium on the corresponding di(bromothienyl)methanes at -70°C gave dilithium derivatives stable at this temperature. Their treatment with anhydrous copper chloride led to the formation of cyclization products with yields no higher than 40% [85, 86].

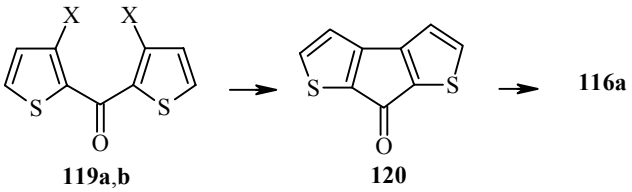


In another paper [87] 7H-thieno[3',2':3,4]cyclopenta[1,2-*b*]thiophene (**116a**) was obtained from bis(3-bromo-2-thienyl)methane and hexamethylditin in the presence of $Pd(PPh_3)_4$. The authors suggest the following mechanism: Oxidative addition of the Pd(0) complex at the C–Br bond followed by transmetallation, leading to the formation of the distannylated derivative **118**; further reductive elimination of the tin leads to ring closure.



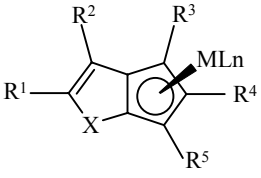
A fundamental and very important shortcoming of the method is the need to use expensive and exotic reagents, such as $Pd(PPh_3)_4$ and $Me_3SnSnMe_3$.

The second method involves synthesis of the cyclic ketones from di(halothienyl) ketones by the Ullmann reaction in the presence of activated copper powder in DMF followed by their reduction to thienocyclopentathiophenes [88]. The yield of the cyclic ketones depends directly on the nature of the halogen and amounts to ~50% in the case of the bromine derivatives and ~100% in the case of the iodine derivatives. Kizhner–Wolff reduction of all the obtained dithiophenocyclopentenones with hydrazine in the presence of potassium hydroxide leads to the corresponding thienocyclopentathiophenes with yields of ~40%.



119 a X = Br, **b** X = I

4. ORGANOMETALLIC DERIVATIVES OF HETARENOCYCLOPENTADIENES

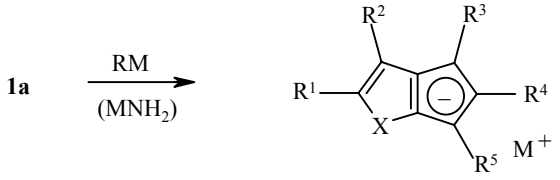


X = O, S, NR

The organometallic derivatives of hetarenocyclopentadienes have been described very little in the literature, and this is clearly due to the poor accessibility of these compounds by synthesis. However, increased interest in this type of compound has been observed recently, since as shown in a series of papers they have good catalytic characteristics in various reactions, e.g., in the polymerization of olefins (M = Ti, Zr, Hf) [89, 90].

The organometallic derivatives of hetarenocyclopentadienes can be divided into two groups, the i.e., organometallic derivatives of hetarenocyclopentadienes with nontransition and with transition metals.

First we will consider the organometallic derivatives of hetarenocyclopentadienes with nontransition metals. Hetarenocyclopentadienes react with the amides of alkali metals or with organometallic derivatives to form a hetarenocyclopentadienide anion, and they therefore exhibit the characteristics of the cyclopentadiene [5-7].

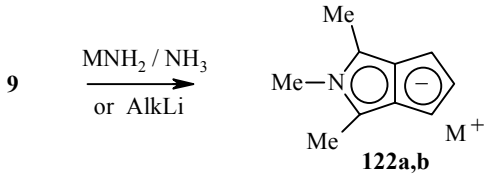


121

R = Alk, Ar; M = Li, K, Mg; X = O, S, NR

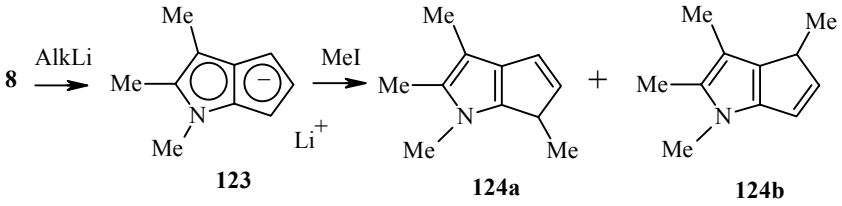
The cyclopentadienide anion can react with a whole series of electrophilic reagents. The direction of attack by the electrophilic reagents is determined in most cases by steric factors. In cases where the steric factors do not have a deciding effect a mixture of compounds is usually formed.

Dihydroazapentalenes readily undergo metallation both by sodium and potassium amides in liquid ammonia and by organolithium compounds with the formation of an azapentalenide anion [5, 17], attack on which by electrophilic reagents always leads to the formation of a mixture of compounds **124a**,**b**.



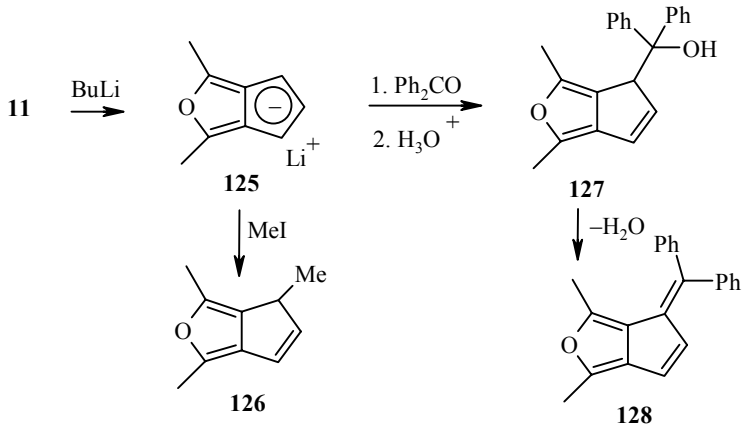
122a,b

122 a M = Na; **b** M = K

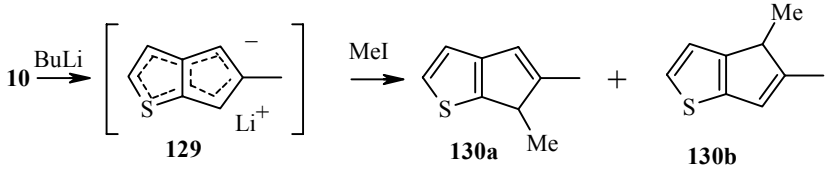


123 **124a** **124b**

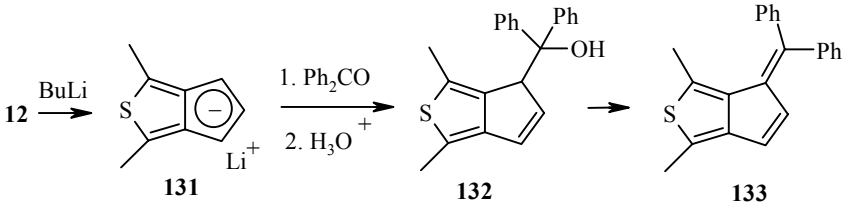
The pentalenide anion, produced by treating 1,3-dimethyl-4H-cyclopenta[*c*]furan (**11**) with butyllithium in ether, reacts with a whole series of electrophilic reagents such as methyl iodide, heavy water, and benzophenone [6], forming compounds **126** and **127** with high yields, while the direction of addition is the same in all cases. In the case of benzophenone the initially formed tertiary alcohol **127** readily loses water and is converted into diphenylfulvene **128**.



The metallation of cyclopentathiophenes with butyllithium in ether, as also with alkali metal amides in liquid ammonia, leads to the formation of a 10π-electron anion [7, 91], which as noted by the authors is stable for a week at -78°C. In the case of compound **10** it was shown that the electrons of the thiophene and cyclopentadiene rings in the obtained anion **129** are delocalized. The reaction of the obtained anion with methyl iodide and heavy water leads to the formation of two regioisomers **130a**,**b**.



The cyclopentadienide anion **131**, produced from 1,3-dimethyl-4H-cyclopenta[*c*]thiophene (**12**), reacts with benzophenone like the 2-oxapentalenide anion described above [91], forming initially the tertiary alcohol **132**, which is converted into the corresponding diphenylfulvene **133**, readily losing water during treatment with *p*-toluenesulfonic acid in benzene.



When treated with such electrophilic reagents as Me_3SiCl, Me_3SnCl, Ph_3SnCl, and Ph_3PCl, thiopentalenyllithium **134**, produced by treating 5-methyl-2-ethylcyclopenta[*b*]thiophene with butyllithium in ether, forms the corresponding heteroorganic compounds [92]. The yields of these compounds in relation to the electrophilic agent are given in Table 4.

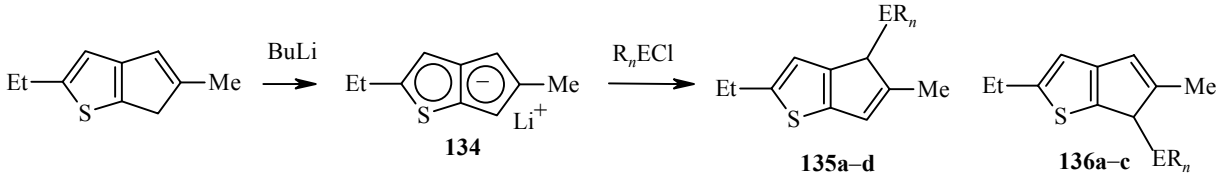
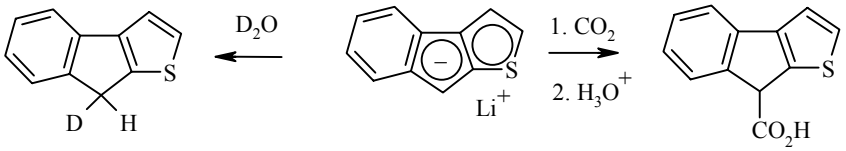


TABLE 4. The Yields of the Compounds and the Ratios of the Isomers

R_nECl	Compound		Ratio	Total yield, %
Me_3SiCl	**135a**	**136a**	1:2	74
Me_3SnCl	**135b**	**136b**	1:2	—*
Ph_2PCl	**135c**	**136c**	1:1	77
Ph_3SnCl	**135d**	—	—	74

* According to $^{119}Sn\{^1H\}$ NMR data; the compounds were not isolated in the individual state by the authors.

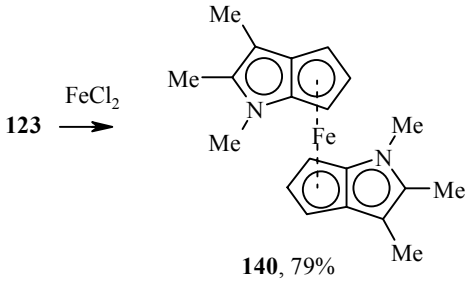
In the case of indenothiophenes metallation of all the compounds takes place exclusively at the methylene bridge with the formation of the anion **137**, as was established from the results of reaction of the lithium derivatives with CO_2 and D_2O (with the exclusive formation of compounds **138** and **139**) [70-72].



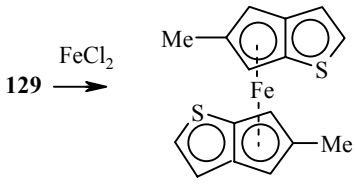
139 **137** **138**

Considerable attention has recently been paid to the synthesis of the organometallic derivatives of hetarenocyclopentadienes with transition metals since changes in the structure of the annelated heterocycle can affect to a significant degree the electronic structure of the cyclopentadiene and, consequently, the properties of the complex.

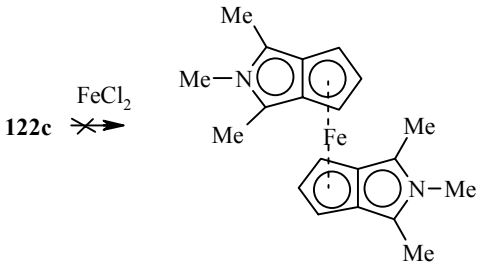
The ferrocenes **140** and **141**, from the lithium derivatives **123** and **129**, are only stable in solution and decompose during attempts to isolate them in the individual state [93, 94]. At the same time it was shown that the isomeric trimethylazapentalenide anion **142** does not react with $FeCl_2$ under the same conditions, and the corresponding ferrocene is not formed.



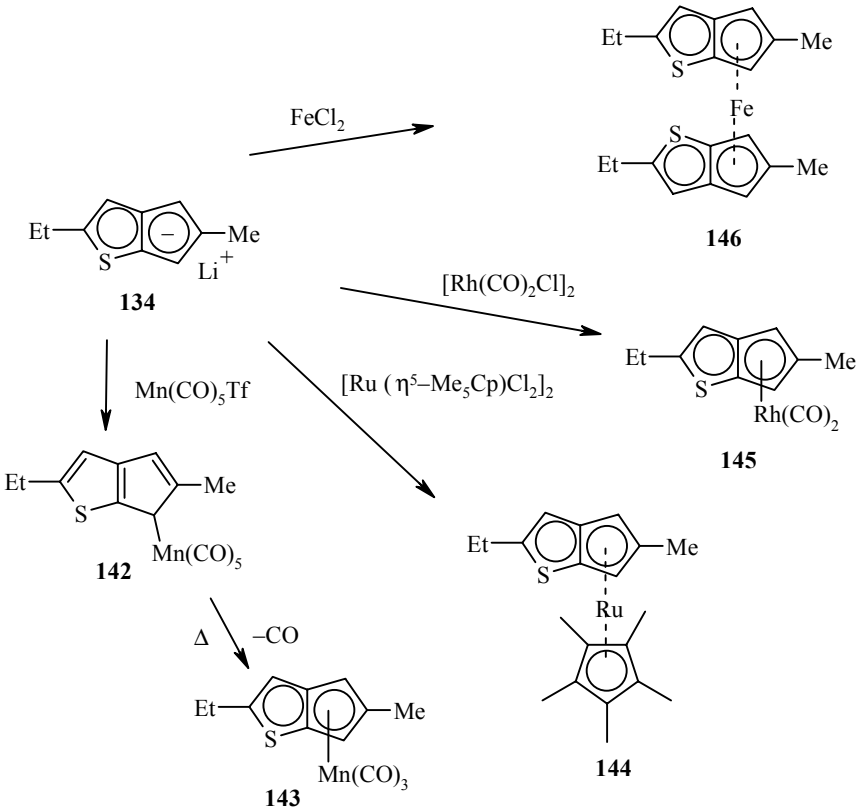
140, 79%



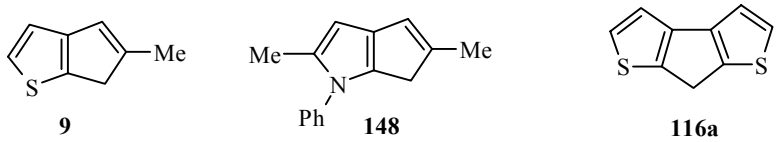
141, 67%



The synthesis of a series of π-complexes containing 2-ethyl-5-methylcyclopenta[*b*]thienyl ligands, with such metals as Mn, Rh, Fe, and Ru has been described [95]. Compounds **142**-**146** were obtained from the anion **134** and the corresponding derivatives of the above-mentioned metals.

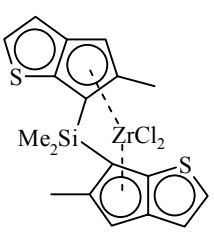


Extremely important is the paper [94] devoted to the synthesis of zirconocenes based on heterocyclylcyclopentadienes [94]. The authors used the following ligands as models:

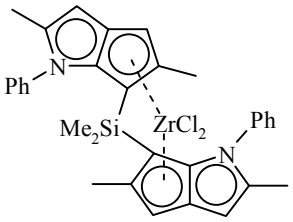


Metallocenes based on the transition metals of group 4 are stable even in the presence of a considerable amount of methylalumoxane (MAO). Such complexes exhibit high activity and stereospecificity in the polymerization of propylene. In addition to the unbridged metallocenes, metallocenes of the *ansa* type were

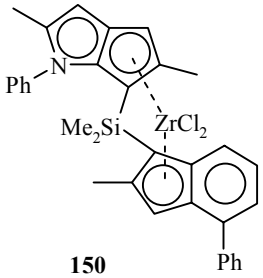
synthesized from the above-mentioned ligands **11**, **147**, **116a** by the usual procedures for indene and fluorene. Symmetrical ligands with a silicon bridge were obtained by the reaction of lithium derivatives with Me_2SiCl_2, and ligands with a carbon bridge were obtained by the reaction of the lithium derivatives with the respective fulvene.



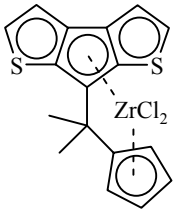
148



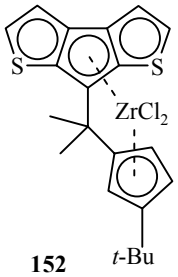
149



150

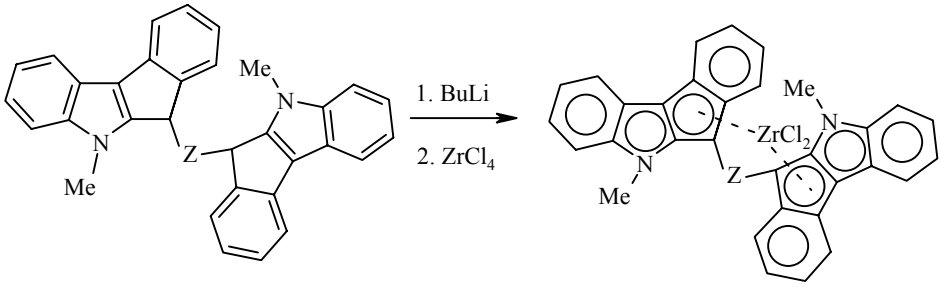


151

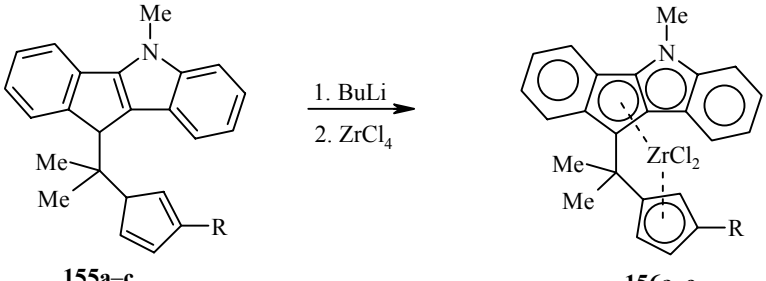


152

A synthesis of the organometallic compounds **154a**,**b** based on indenoindole ligands containing various substituents both in the indene and in the indole ring was presented in [90]. Methods for the production the bridged compounds **153a**,**b** and **155a-c** were similar to those described above [89], and symmetrical ligands with a carbon bridge were obtained in addition to symmetrical ligands containing a silicon atom in the bridge.



153 a Z = CH_2; **b** Z = $SiMe_2$ **154 a** Z = CH_2; **b** Z = $SiMe_2$



155a–c **155, 156 a** R = H; **b** R = Me; **c** R = *t*-Bu **156a–c**

It was shown that the metallocene catalysts **154a**,**b** were extremely active in the polymerization of ethylene.

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