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SYNTHESIS OF PHOTOCHROMIC DIHETARYLETHENES.* (REVIEW)

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The main methods of synthesis of dihetarylethenes are given in the review. Approaches for obtaining photochromic compounds are discussed, in which both the traditional residues of perfluorocyclopentene, maleic anhydride, and maleimide, and little-studied fragments of partially saturated or aromatic heterocycles are used as the ethenic fragment. Significant attention is paid to the X-ray structural data of open and cyclized forms of the photochromes.

Keywords: diarylethenes, dihetarylethenes, dithienylethenes, photochromes, thermally irreversible photochromes, photocyclization, photochromism in the crystalline phase, optical memory, information storage.

Photochromism is defined as the reversible conversion induced by light of a substance **A** (photochrome) into product **B** differing in absorption spectrum (color) and internal energy, dielectric constant and other physicochemical parameters [1].

$$\mathbf{A} \underset{h\nu_1}{\overset{h\nu}{\rightleftarrows}} \mathbf{B}$$

Photochromic materials are used widely. Protective sunglasses are an example of their practical use. Photochromes are also used in actinometers, dosimeters, various optoelectronic equipment, etc. [2]. In recent times they are being considered as extremely promising systems to store information. Of course the properties of such photochromes must be satisfactory for the majority of different requirements, among which are a high reaction rate under the action of radiation, separation of the absorption bands of the open (**A**) and cyclized (**B**) forms, solubility in organic solvents to prepare films, the ability for photochromic conversion not only in solution but also in the solid state, availability and relative cheapness of the material, etc. In addition, there are two fundamental qualities enabling photochromes to be used as optical memory elements.

The first of these is characteristic for many materials and devices and is defined in the English-language scientific literature as "fatigue resistance" – resistance to fatigue. Fatigue resistance applied to photochromes is defined as the number of interconversion cycles of forms **A** and **B** on irradiation corresponding to decomposition of 20% sample [3]. Of course in actual systems the fatigue resistance of photochromes must consist of thousands of units. The second fundamental property determining use is the thermal irreversibility of

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* To the one hundredth birthday of Professor Ya. L. Gol'dfarb.

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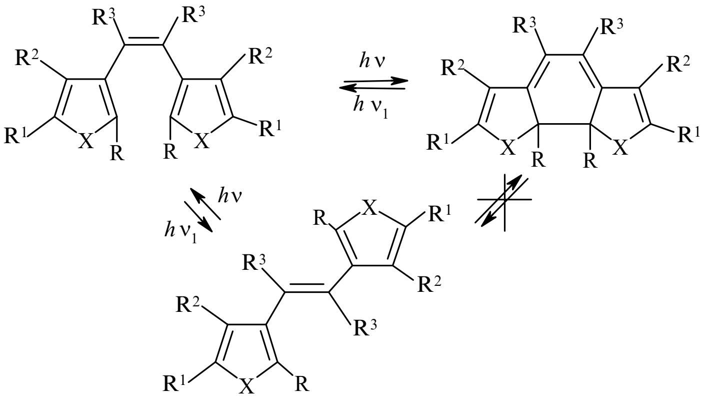
the photoconversion, which is specific for photochromes. The overwhelming majority of photochromes transfer from one form to the other even in the absence of radiation, which hinders the recording of information on them. Until recently this was an insurmountable obstacle to the use of photochromes as memory elements for optoelectronic devices.

A breakthrough occurred at the end of the eighties of the last century when the Japanese professor M. Irie proposed 1,2-dihetarylethenes as thermally irreversible photochromes [4]. The starting point of his investigations was the study of the photocyclization of stilbene-like aromatic and heteroaromatic compounds in a development of the studies of R. Kellogg on the photocyclization of difuryl- and dithienylethenes (Scheme 1) [5].

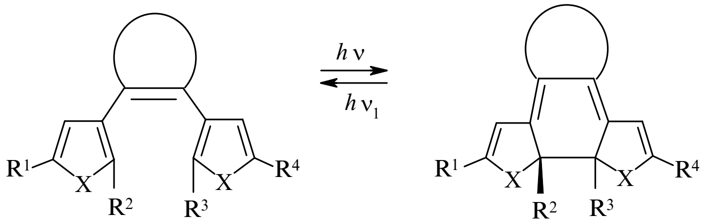
Scheme 1



The phenanthrene products of photocyclization are isomerized to the initial stilbenes even in the dark and their cyclized hetero analogs proved to be far more stable even at elevated temperatures. A theoretical basis for this phenomenon was proposed in [6].

Since the photocyclization of stilbenes and dihetarylethenes is accompanied by *cis-trans* isomerization, during which the *trans* isomers do not give a cyclized form, the next logical step was the closure of the *cis* forms in cyclic ethenic fragments, such as residues of perfluorocyclopentene, maleic anhydride, and maleimide (Scheme 2).

Scheme 2

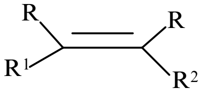


It subsequently turned out that similar photochromes possess not only thermal irreversibility but also a high fatigue resistance, in several cases approaching tens of thousands of cycles. Certain diarylethenes display photochromic activity even in the crystalline phase. Dihetarylethenes such as diindolylfurandiones, patented as typical photochromes [7,8], possess a broad spectrum of biological activity [9-11]. The unique combination of these properties predetermined the exceptional interest in dihetarylethenes during the past decade. Several reviews have been devoted to it, the last of which was published last year [3,6,12-16]. They have mainly focused on the physicochemical and optical data. We therefore considered it expedient to systematize the methods of obtaining dithienylethenes and soon decided on the specifics of their structure. Since some of the results were obtained in the laboratory in which Professor Ya. L. Gold'farb spent half his life, the studies of this collective will be presented in somewhat more detail.

SYNTHESIS OF DIHETARYLETHENES

1. 1,2-Dihetarylethenes

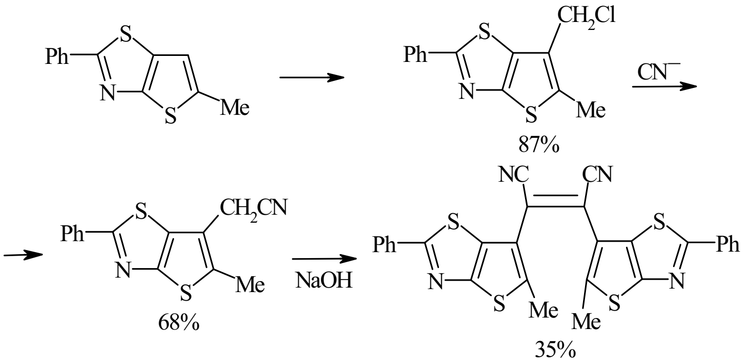
Symmetrical or unsymmetrical dihetarylethenes represented by the general formula below, in which R^1 and R^2 are such heterocycles as thiophene, furan, pyrrole, thiazole, benzothiophene, and indole, are obtained as a rule by combination reactions starting from the corresponding acetyl, cyanomethyl, etc. compounds.



R = H, Alk, CN, COOH, CO_2Alk, F, CF_3

Scheme 3 gives a representation of the most typical approach to the synthesis of dinitrile photochromes, which are the starting materials for a vast range of photochromic products, and have independent interest as well [17].

Scheme 3

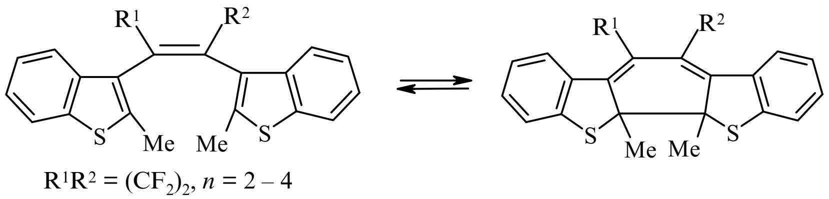


The overall yields here were not high, the unexpected can occur at any stage of the process. The yield of chloromethyl-substituted compound in Scheme 3 was about 90%, but the corresponding selenophene derivative was formed by an analogous scheme in a yield of only 25% [18]. The bottle-neck in the synthesis of dicyanides of the structure indicated is the final stage, *viz.* the coupling reaction in a two-phase system of CCl_4–aqueous alkali solution in the presence of an interphase-transfer catalyst. For example, the final stage of obtaining 1,2-dicyano-1-(2-methylimidazo[1,2-*a*]-3-pyridyl)-2-(2,3,5-trimethyl-3-thienyl)ethene proceeds in 18% yield [19].

2. Dihetarylperfluorocyclopentenes

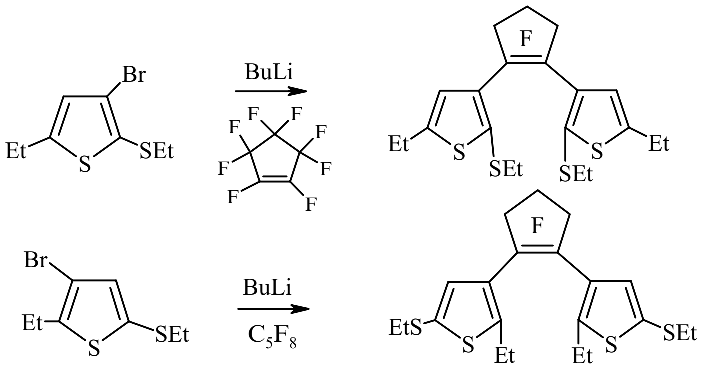
A series of photochromic products in which benzothiophene rings are linked to perfluorocyclenes was described for the first time in [20] (Scheme 4).

Scheme 4

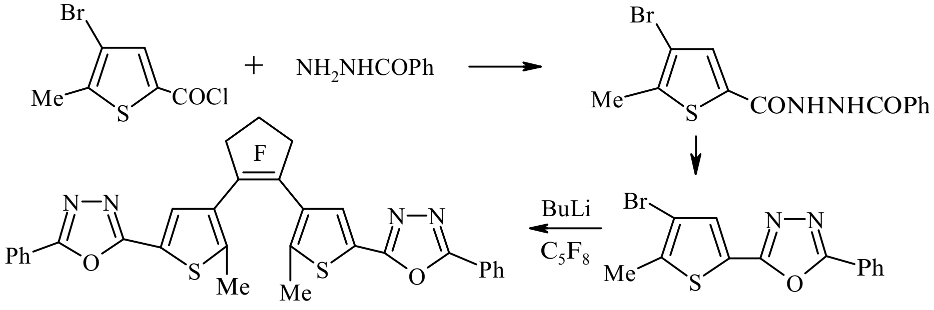


The basic method of obtaining perfluorocyclopentene dihetarylethenes used in the majority of investigations was the interaction of lithium derivatives of thiophene with octafluorocyclopentene (Schemes 5 [21,22] and 6 [23]). The skeleton of the molecule is formed in this way for further functionalization.

Scheme 5

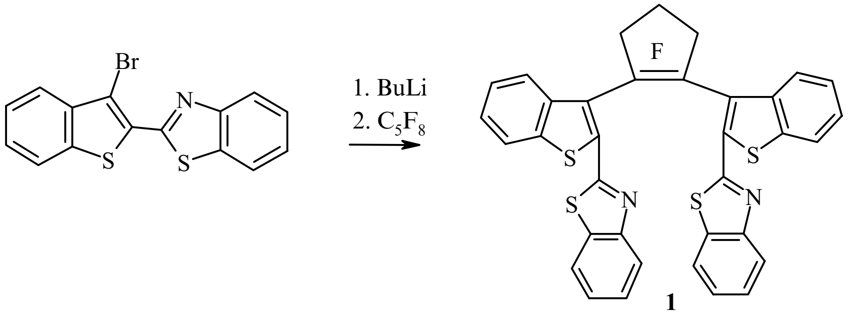


Scheme 6

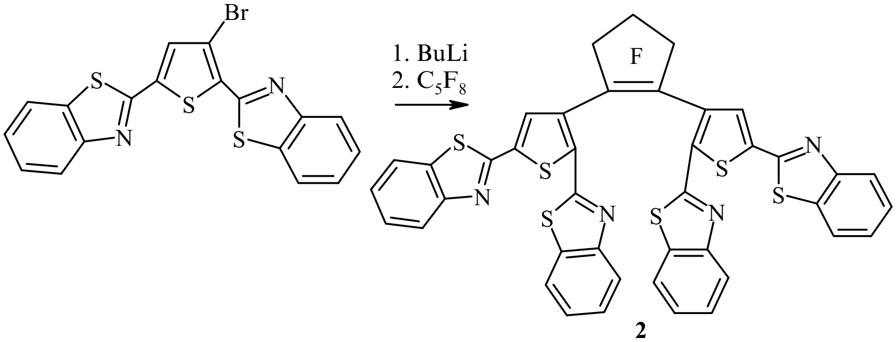


Compounds are formed similarly in which bulky heterocyclic residues are disposed in positions 2 and 2' of the thienyl rings in place of the alkyl groups [24] (Schemes 7 and 8).

Scheme 7



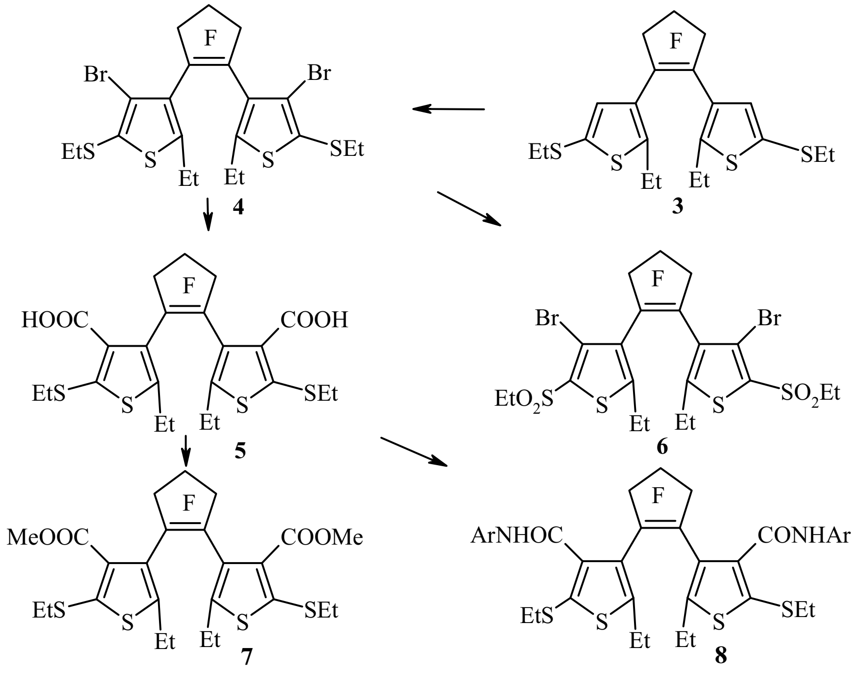
Scheme 8



Both products **1** and **2** possess distinctly marked photochromism which removes the obvious doubts in the possibility of cyclizing what might seem to be such sterically strained molecules.

Methods have been developed [25] for introducing functional groups into positions 4 and 4' of the thiophene rings of symmetrical photochromes (Scheme 9).

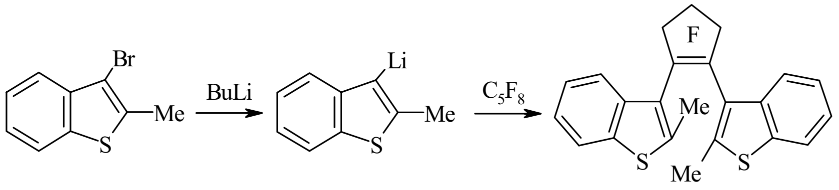
Scheme 9



Products **3-8** are convenient compounds for the subsequent synthesis of photochromes with condensed heterocycles. We note however that the reactivity of the bromine atoms in compound **4** is restricted to a definite extent probably by steric factors. Though lithium and then also carboxyl derivatives are formed in high yield the introduction of formyl groups into positions 4 and 4' by reaction with DMF was unsuccessful. Starting materials and decomposition products were also recorded in attempts to obtain the corresponding aldehydes by other methods.

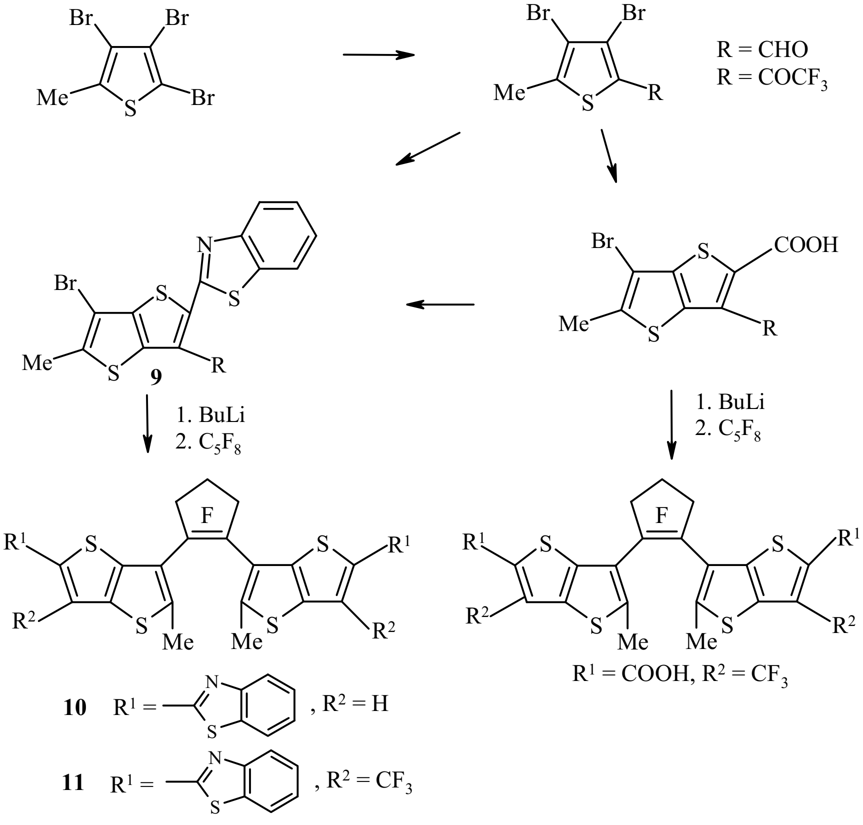
Condensed alkylthiophenes are also used regularly in the synthesis of photochromes (Scheme 10) [20]. In this case reaction occurs with high regioselectivity.

Scheme 10

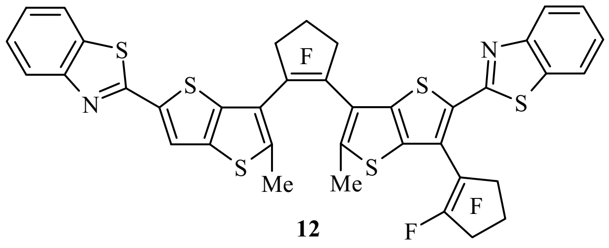


The synthesis of the first representatives of promising photochromes with thienothiophene fragments was proposed in [26] (Scheme 11).

Scheme 11



The authors paid attention to the possible migration of lithium on direct metallation of the bromide **9** or in the resulting photochrome **10**, which is indicated by the appearance of compound **12** in the reaction products.



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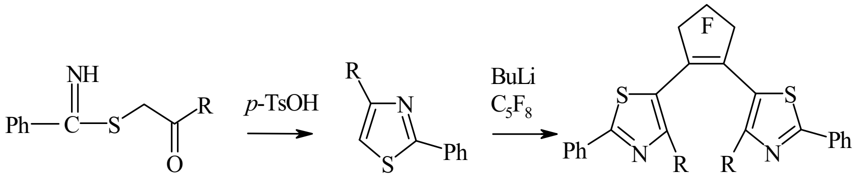
Molecules other than lithium derivatives of thiophene react with perfluorocyclopentene to form photochromes. The synthesis of two bisthiazolylethenes has been described (Scheme 12) [27].

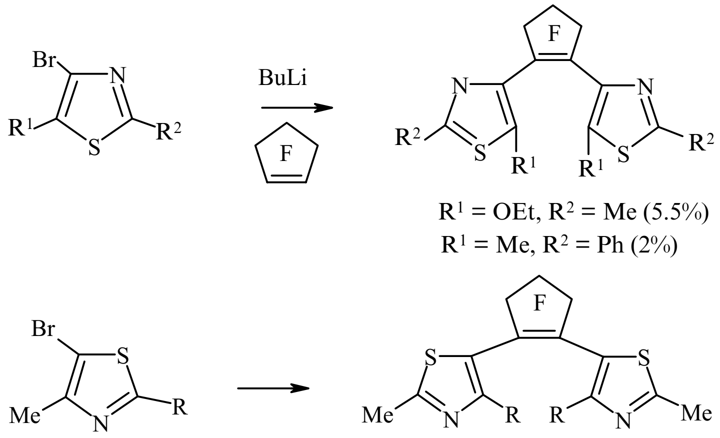
Scheme 12



R = Me (40%), CF_3 (55%)

The preparation of isomeric photochromes from thiazoles is represented in Scheme 13 [28]. The overall yields of products were extremely low and did not exceed 10% for four of the five compounds shown in the scheme.

Scheme 13

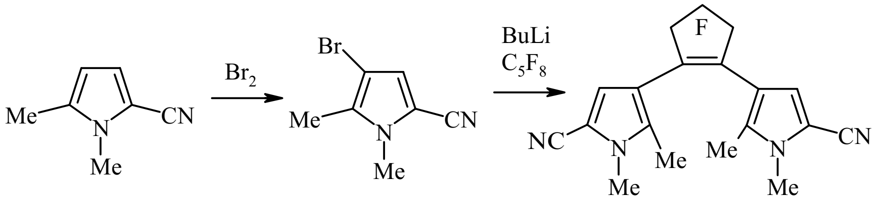


R^1 = OEt, R^2 = Me (5.5%)
R^1 = Me, R^2 = Ph (2%)

R = Me (6%); R = Ph (25%); R = p-$MeOC_6H_4$ (9%)

1,2-Dihetarylethene with two pyrrole rings was obtained by the sequential interaction of the appropriate bromide with BuLi and C_5F_8 in THF in 11% yield (Scheme 14) [29].

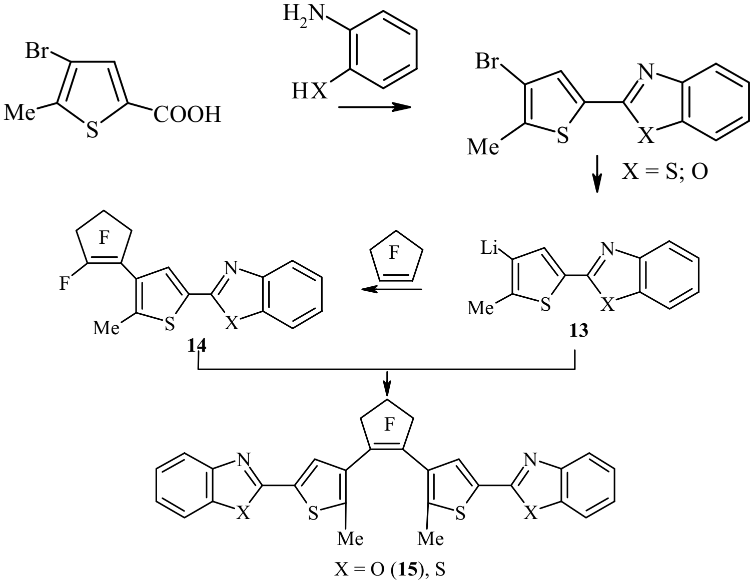
Scheme 14



We note that in all cases substituted heterocycles with functional groups resistant to butyllithium or heteryllithium derivatives were used.

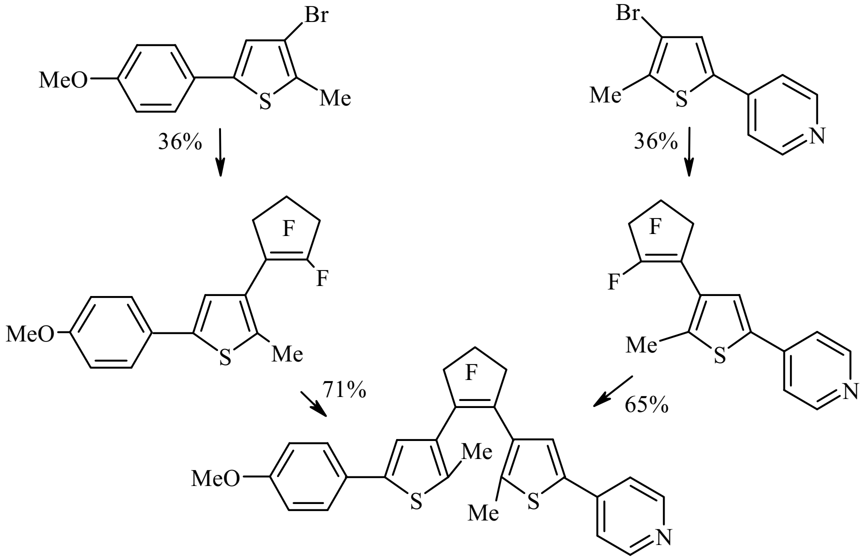
At an equimolar ratio of reactants there is a high probability of forming products of substitution of only one of the fluorine atoms on the double bond of the cyclene. For example the synthesis of the desired product **15** (Scheme 15) was effected either in one stage with a twofold excess of the lithium derivative **13** relative to perfluorocyclopentene or in two stages with the preliminary isolation of the monofluoride **14** [30].

Scheme 15



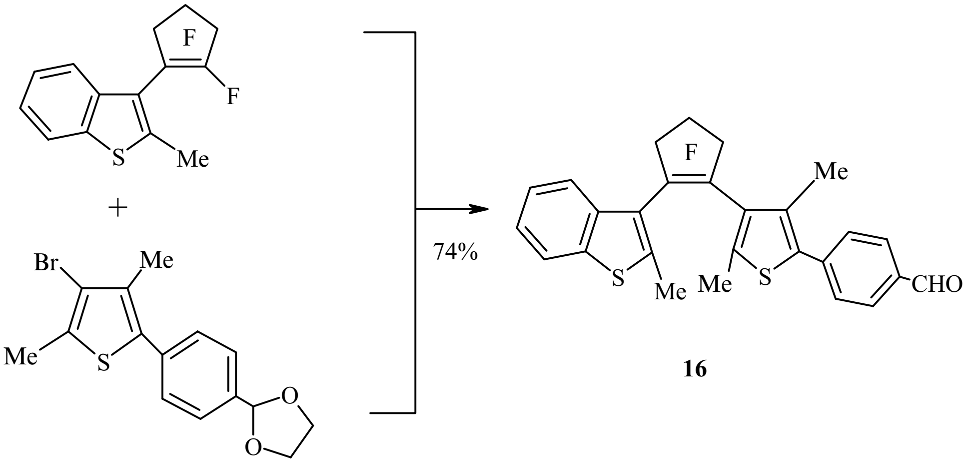
It is important to emphasize that the monosubstitution products may be isolated and involved in further conversions leading to the preparation of photochromes of unsymmetrical structure. An example of the synthesis of the latter carried out in the laboratory of J. Lehn is given below (Scheme 16) [31].

Scheme 16

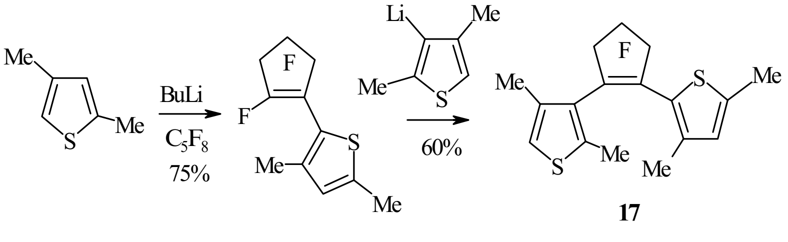


The syntheses of the unsymmetrical compounds **16** (Scheme 17) [32] and **17** are also characteristic examples, in which perfluorocyclopentene is linked with position 2 of one thiophene ring and position 3 of another (Scheme 18) [33].

Scheme 17

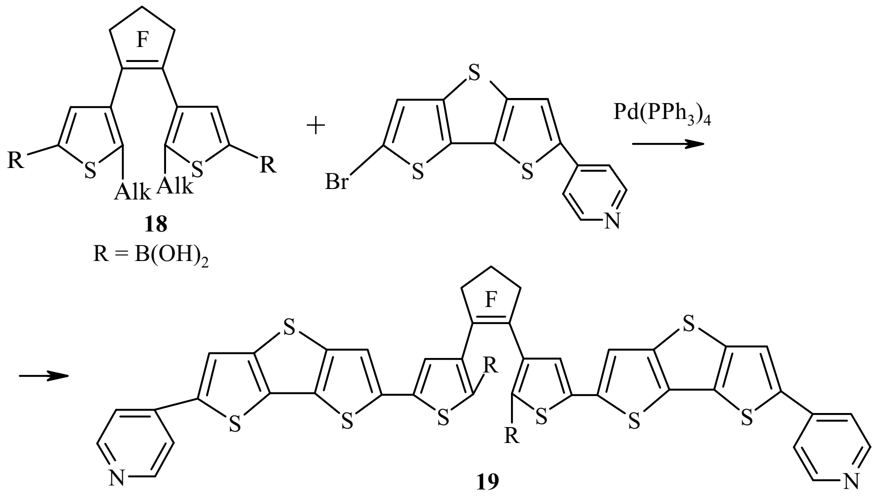


Scheme 18



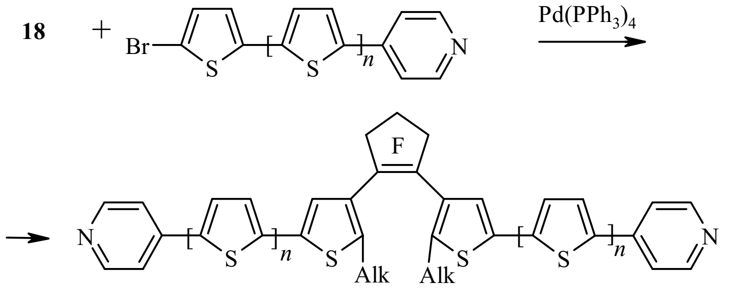
The preparation of dithienylethenes of complex structure comprises mainly the functionalization of previously obtained dithienylethenes of, as a rule, exceptionally simple structure. In Scheme 19 is given a fragment of the synthesis (more precisely, assembly) of the unique photochrome **19**, carried out by J. Lehn and co-workers [34].

Scheme 19



The dithieno[3,2-*b*:2'3'-*d*]thiophene system, the nodal fragment of product **19**, was first synthesized in the laboratory of Y. L. Gol'dfarb [35]. Step-by-step building up of the chain in the dithienylethene **18** using the Sudzuki reaction leads to the creation of polythienyl photochromes (Scheme 20). Similar oligomeric products were also described in [36]. The synthesis and properties of a polymer produced with a photochromic dihetarylethene fragment in the main chain are given in [37].

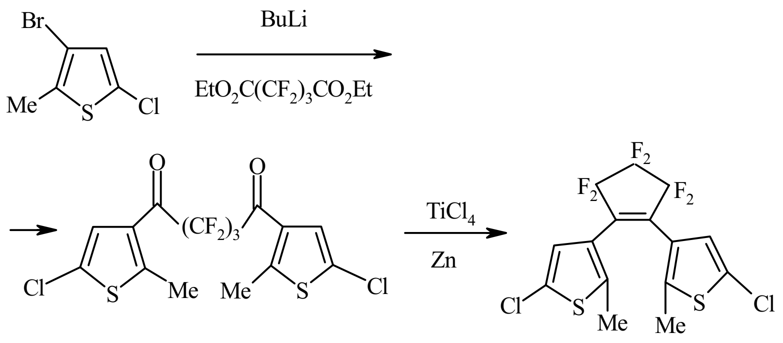
Scheme 20



Alk = C_6H_{13}, *n* = 2, 3

On the whole it is probably possible to regard photochromes based on perfluorocyclopentene as being accessible. The yields of the latter at the final stage of the process reached almost 80%. Nevertheless search is continuing for new approaches to a photochrome with a hexafluorocyclopentene fragment. A publication appeared recently [38] describing a fairly general method of synthesis of 1,2-diarylperfluorocyclopentenes based on the use of hexafluoroglutaric acid diethyl ester as starting material (Scheme 21). The authors asserted that the formation of a dithienyl ketone and cyclization into the final product was effected in yields of 70 and 55% respectively. The advantages of the method are difficult to assess from one publication, although one is undoubtedly the relative availability of perfluoroglutaric acid.

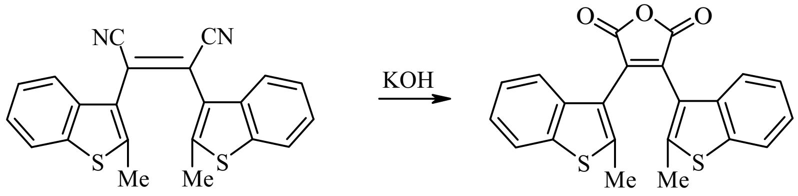
Scheme 21



3. Diarylmaleic Anhydrides

The synthesis of dithienyl photochromes with a residue of maleic anhydride (furan-2,5-dione fragment) as ethylene bridge is not a simple problem. The vicinal dinitriles mentioned in Chapter 1 serve as starting materials. It must be borne in mind that maleic anhydride gives the latter only in the *cis* conformation. Separation of *cis* and *trans* isomers is an additional difficult problem. A typical synthesis of photochromes from cyanides is shown in Schemes 22 [39] and 23 [4].

Scheme 22

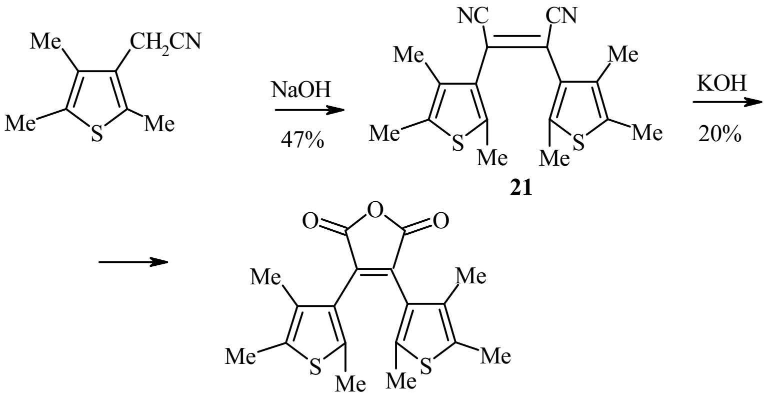


20 14%

Cyclization into the maleic anhydride derivative **20** occurs in a yield of only 14%. It must not be forgotten that the overall yield of the initial dicyanide (Scheme 3) was about 25% calculated on 2-methylbenzothiophene.

The 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**21**) obtained in 47% yield was hydrolyzed in alkaline solution with the formation of the maleic anhydride derivative **22** (20%).

Scheme 23



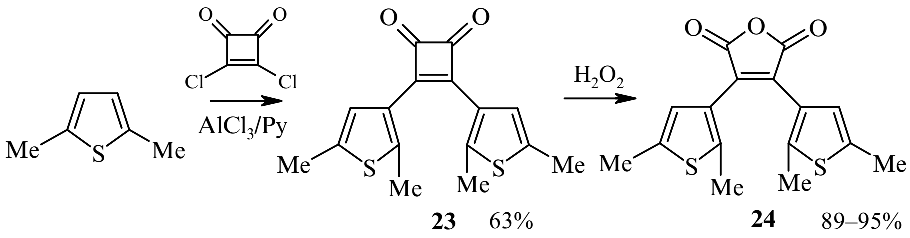
21

22

The total yield of the desired product **22** calculated on the initial trimethylthiophene was only about 4%. Similar yields are characteristic for all cases of the preparation of photochromes based on maleic anhydride, which makes the search for more efficient methods of creating them extremely pressing.

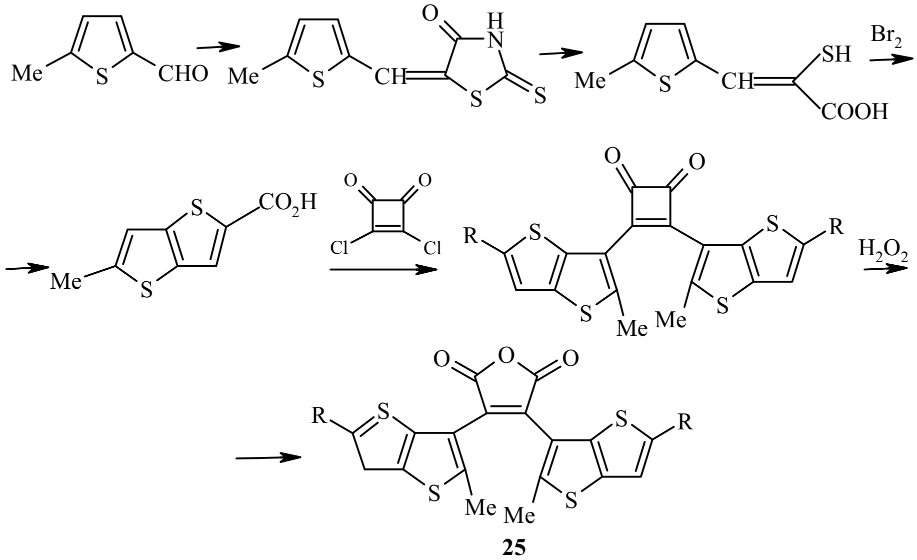
The original means of synthesizing photochrome **24** (Scheme 24) was proposed in [40,41].

Scheme 24



The first step in the process is the synthesis of 1,2-bis(2,5-dimethyl-3-thienyl)cyclobutene-3,4-dione (**23**) by the acylation of 2,5-dimethylthiophene with 1,2-dichlorocyclobutene-3,4-dione in the presence of aluminum chloride and pyridine [42]. The resulting diketone **23** was oxidized according to Baeyer–Villiger with 90% hydrogen peroxide in acetonitrile (95% yield) or with 35% hydrogen peroxide in CH_3CN with a catalytic amount of *p*-toluenesulfonic acid (89% yield). The method is general and was applied successfully to the synthesis of photochrome **25** with condensed thieno[3,2-*b*]thienyl fragments (Scheme 25) [43].

Scheme 25

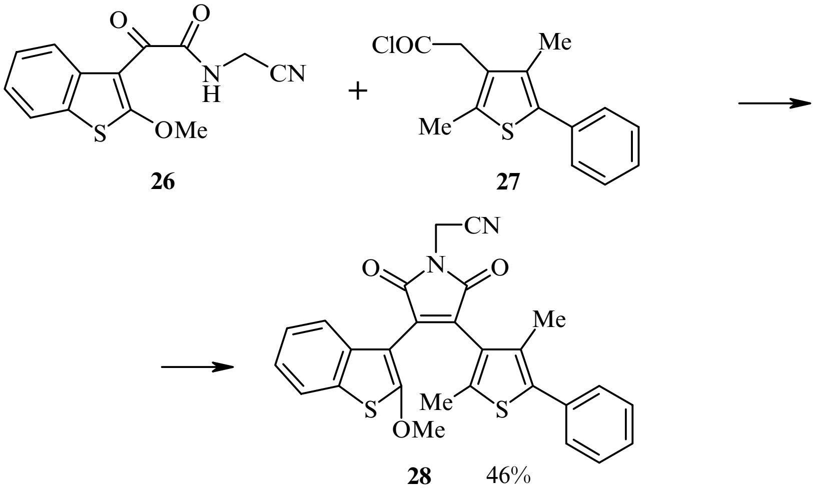


Since the squaric acid chloride is a commercial reagent it may be said that, thanks to the method given, photochromes with a maleic anhydride fragment as the ethene bridge prove to be relatively accessible. It is easy to contemplate the expediency of further functionalization of the latter, particularly the synthesis of maleimide photochromes from them.

4. Diarylmaleimides

Syntheses of photochromes described in the literature in which the heterocycles are separated by a maleimide ring are probably no less laborious than the preparation of compounds based on maleic anhydride. A general approach has been developed towards constructing these compounds, which is illustrated in Scheme 26 for the example of the synthesis of the unsymmetrical photochrome **28** [44]. Thus treatment of 2-methoxybenzothiophene with oxalyl chloride and aminoacetonitrile gives 3-[N-(cyanomethyl)oxamoyl]-2-methoxybenzothiophene (**26**). In its turn 2,4-dimethylthiophene was converted in an overall yield of less than 5% into the acid chloride **27**, which reacts with compound **26** forming the photochromic product **28**.

Scheme 26



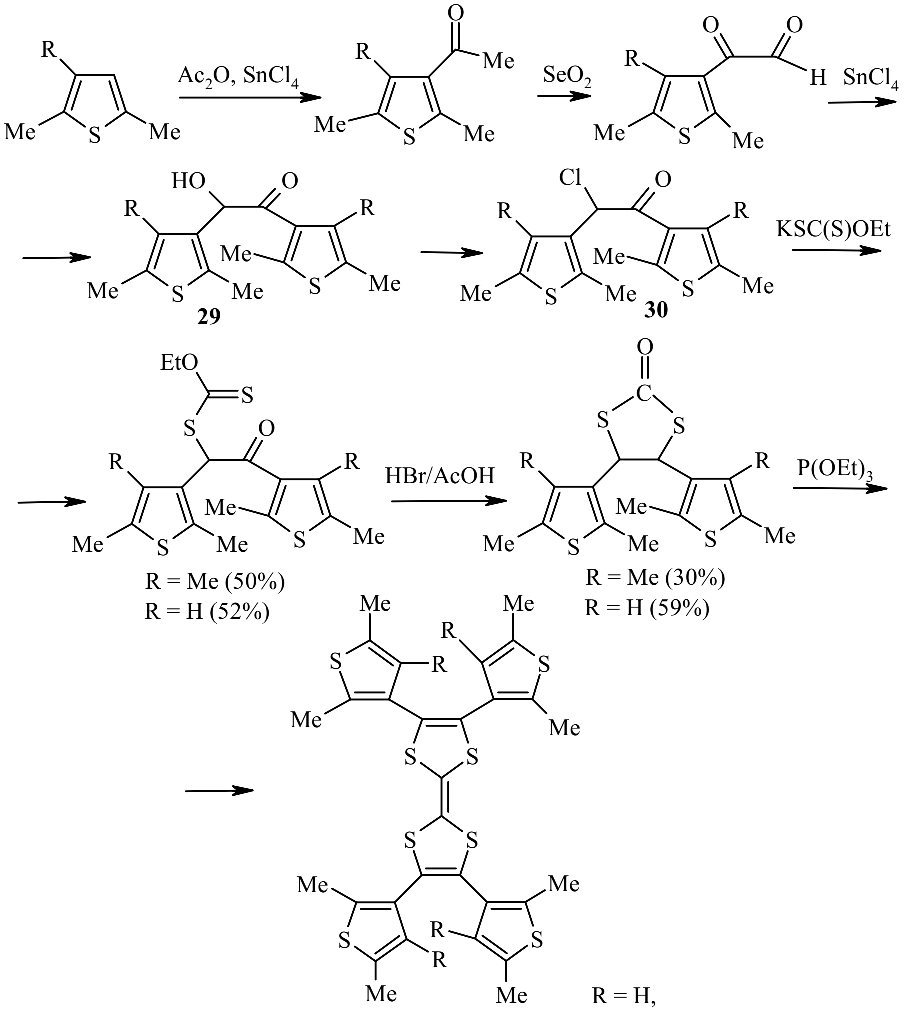
Diarylmaleimides with optically active *L*- and *D*-menthyl groups in position 2 of the benzo[*b*]thiophene residue were obtained by a similar scheme [45].

Overall it may be said that short bridges are characteristic of all the methods of synthesis described in sections 1-4. These problems have stimulated authors to search persistently for approaches to photochromic dihetarylethenes with new ethenic bridges.

5. Synthesis of Photochromes with New Ethenic Fragments

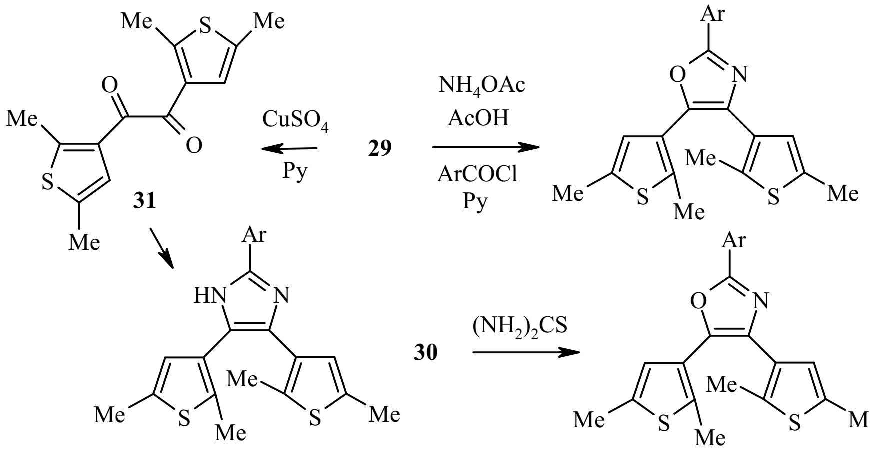
Much more attention has been paid in recent years to the synthesis of compounds in which the thiophene rings are linked by heterocyclic fragments of the type of dithienylmaleimide or dithienylmaleic anhydride. The preparation of tetrathiafulvalenes with photochromic dithienylethene fragments is shown in Scheme 27 [46].

Scheme 27

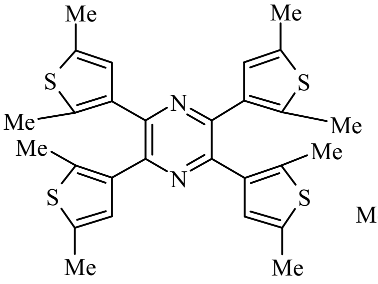


Compounds **29** and **30** (R = H) proved to be universal precursors of structures with diazine, triazine, and azole rings as ethenic bridges. Thus a wide set of dithienylazoles with photochromic properties was obtained from acyloin **29** (Scheme 28) [47,48].

Scheme 28



An analogous approach was extended to the synthesis of compounds with diazines **32,** and also with the fundamental heterocycles **33** and **34,** as the ethenic components [49].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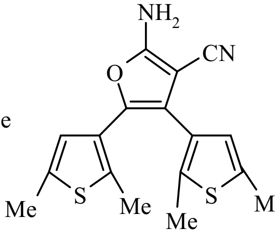
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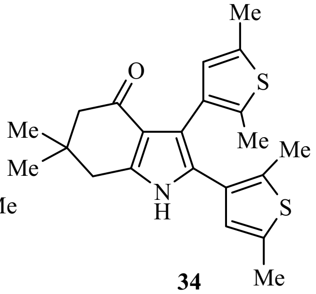
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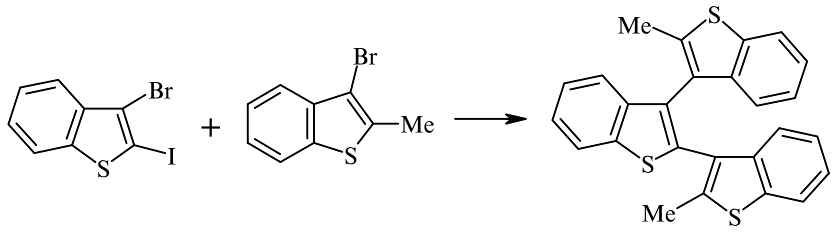
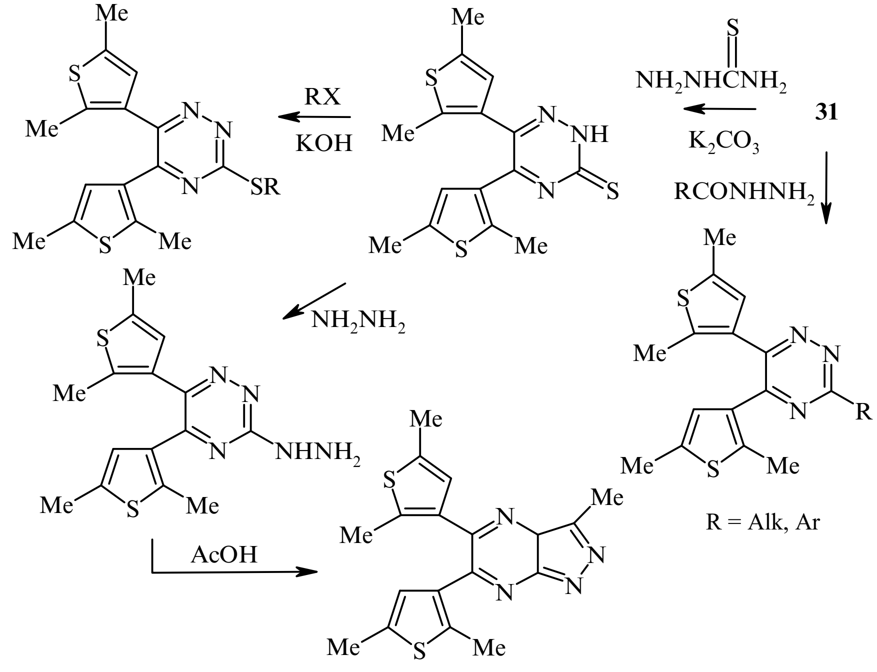
Compounds close in structure were proposed in a patent [50] as photochromes with good operating properties (Scheme 29).

Scheme 29



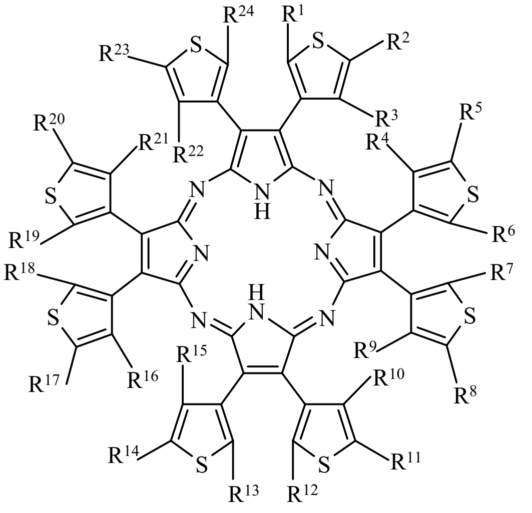
The synthesis of a whole series of triazines was effected from diketone **31** according to Scheme 30 [51].

Scheme 30



The accumulated data permit the statement that the introduction of electron-deficient diazines and triazines inhibits the development of photochromic properties in dihetarylethenes. On the other hand the presence in the latter of electron-rich azoles and fundamental heterocycles as "little bridges" favors the development of photochromism. It must also be kept in mind that the introduction of electron-withdrawing substituents into the dihetarylethenes depicted in Scheme 28 leads to a loss of photoreversibility.

Among the photochromic products, which are potential carriers of information, compounds **35** [52,53] containing several dithienylethene fragments have been patented.

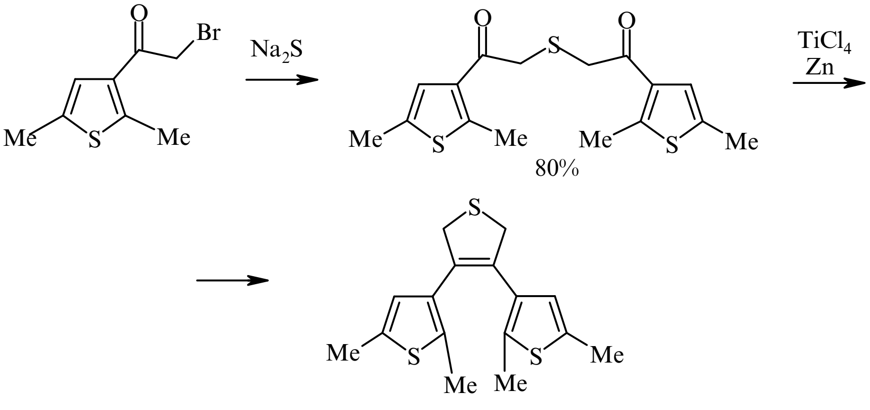


35

The authors of a method of synthesis of perfluorocyclopentene photochromes from perfluoroglutaric acid proposed [54] the construction of their nonfluorinated analogs. The synthetic scheme practically repeats Scheme 21, however here the yield of final product was no more than 20%, which as usual makes urgent the search for convenient general methods of synthesis of photochromes with new ethene fragments.

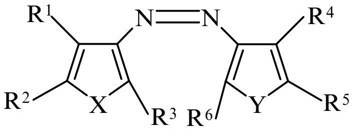
Regretably, low yields also applied in the method of obtaining photochrome **36** with a dihydrothiophene bridge [55] (Scheme 31).

Scheme 31



36

In the series of patents a certain attention is paid to azo compounds **37**, which can be considered as analogues of dihetarylethenes containing azo groups as the bridges [56-58]. These conpounds have pronounced photochromic properties, however their usage perspectives are not clear due to problem of *E*,*Z*-isomerism mentioned above.



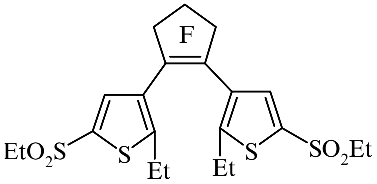
37

The search for new ethenic fragments and the improvement of the methods of synthesis of existing types of photochromes continue to be urgent problems of dihetarylethenes. We emphasize that up to the present time dihetarylethene derivatives with three different types of ethenic fragment have been studied in practice. These are perfluorocyclopentenes, furan-2,5-diones, and maleimides. The differences in their structures do not deprive them of the fundamental properties inherent of diarylethenes, *viz.* thermal irreversibility and high fatigue resistance.

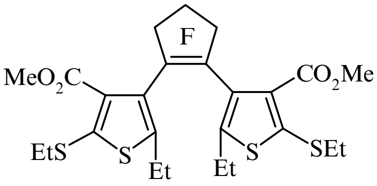
ABSORPTION SPECTRA OF DIHETARYLETHENES AND X-RAY STRUCTURAL DATA

Information on the optical and photochromic properties of dihetarylethenes accompanies their synthetic data in the majority of cases. Open forms of dihetarylethenes have, as a rule, absorption maxima in the 250-350 nm region, cyclized forms at 500-600 nm. With a selection of electron-donating and electron-withdrawing substituents the absorption maximum of form **B** may be displaced to 828 nm [59]. The overwhelming majority of dithienylethenes possess thermal irreversibility. However the accumulation of electron-withdrawing groups in photochrome molecules reduces the stability of the cyclized forms [59,60]. Bulky substituents in positions 2 and 2' of the thiophene rings also assist thermal reversibility [61]. The thermal instability of photochrome **2** is probably determined by a combination of both factors. The open and closed forms of product **1** do not undergo change in the dark even on heating and the cyclized form **B** of photochrome **2** is converted into the open form even at room temperature.

In spite of the large number of photochromes synthesized recently, their spatial structure has been studied little. The most important and unambiguous information is provided by X-ray structural analysis since in real optical systems photochromes will be in the solid state, most likely in a film either as a mechanical ingredient or as a chemically grafted fragment. The data of X-ray structural analysis for dithienylethenes acquire more importance than the more numerous communications on their photochromism in the crystalline phase [62]. The structure of compounds for which actual atomic coordinates have been established are considered below. The perfluorocyclopentene bridges in these compounds are either flat (compounds **38**, **39**) or have the form of an envelope with deviation of the apex from the plane of the remaining four atoms of no more than 0.4 Å (**7**, **15**) [25,63].

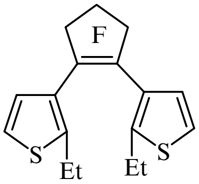


38

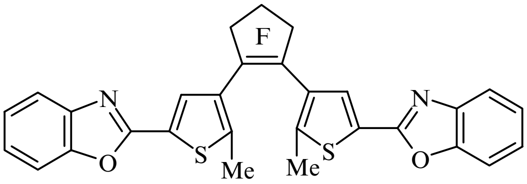


7

A characteristic of all the compounds considered in the open form **A** is a significant twist of the thienyl rings (**T**) relative to the plane of the perfluorocyclopentene, maleic anhydride, and cyclobutenedione. Their absolute values differ significantly. For example, for the sulfonyl derivative **38** the dihedral angle between these planes is 56.2°, which is insignificantly different from the analogous angles in the structures of **39** (55.9; 59.6°) and **15** (54.5; 53.1°). The angles indicated were close to 90° for ester **7**, and in anhydride **24** the thiophene planes were unfolded relative to the furandione ring by approximately 47° [41]. A similar noncoplanarity also causes the absence of a general chain of conjugation in the open forms of the dithienylethenes.



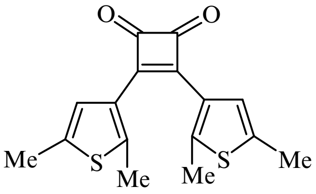
39



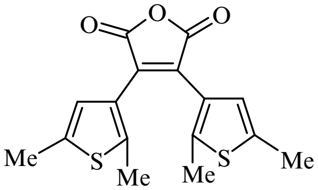
15

A local conjugation arises on introducing the aromatic benzoxazole ring at positions 5 and 5' of the thiophene nuclei (photochrome **15**). In this case the thiophene and benzoxazole fragments are coplanar. However we emphasize that the conjugated chains in these fragments are not extended to the double bond of the fluorinated cyclene [63]. The lengths of the double bonds in perfluorocyclopentene and maleic anhydride in these photochromes do not differ from standard mean statistical values.

In connection with this attention is drawn to the data of X-ray structural analysis of the open form of 1,2-bis(2,5-dimethyl-3-thienyl)cyclobutenedione **23** [41]. Firstly, the thiophene rings in this compound are turned relative to the plane of the four-membered ring by different angles (22.00° and 36.78°), though both angles and the dihedral angle between the thiophene rings $\mathbf{T^1/T^2}$ (47.89°) proved to be the minimum of all the angles found in the structures described.



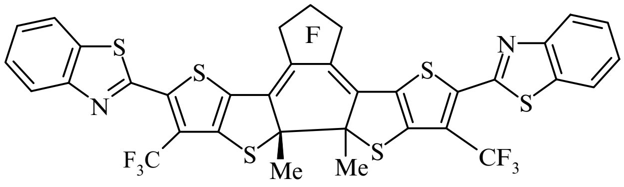
23



24

Secondly, attention is drawn to the length of the double bond in the four-membered ring (1.387 Å) which is significantly longer than the analogous bond in hexafluorocyclopentene and furandione fragments. In all the forms **A** of the photochromes given above the length of the double bond does not exceed 1.33 Å. These facts in our view indicate the partial conjugation of the double bond of the cyclobutene fragment with the thiophene ring, which increases the energy of the aromatic system, adding to the conformational stability of the open form **23A** both in solution and in the crystal and impedes cyclization on photoirradiation [41] (cf. [64,65]).

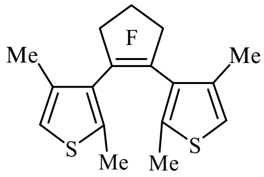
The spatial structure of photochromes of form **B** has been little investigated. This is mainly linked with the difficulty of separating the enantiomers and obtaining monocrystals suitable for X-ray analysis. We decided on the structure of 1,2-bis[2-methyl-5-(2-benzothiazolyl)-6-trifluoromethylthieno[3,2-*b*]-2-thienylperfluorocyclopentene (**11**) [26].



11B

The fluorinated ring **F** in this photochrome has the form of an envelope the apex of which deviates from the plane by -0.380 Å. The thienyl fragments lose their aromaticity and also assume the conformation of envelopes. The six-membered ring formed acquires the conformation of a "twisted sofa" with *trans*-orientated methyl substituents at positions 2 and 2'. The main skeleton of the molecule (except for the fluorine atoms) is practically planar since the dihedral angles between the planes of the rings do not exceed 3.27°. The alternation of bond lengths of different degrees of multiplicity in the chain –C(4)–C(3)–C(1")–C(2")–C(3')–C(4')– indicates the formation of a new conjugated system of the polyene type.

Reversible photochromic conversions in the crystalline phase have been studied for compounds **40** and **41** [66,67]. The molecule of **41B** [67] is constructed similarly to **11B**. All the five-membered rings have the conformation of envelopes, the six-membered ring has the conformation of a "twisted sofa". The sizes of the dihedral angles $\mathbf{T^1/F}$ (-12.14°), $\mathbf{T^2/F}$ (11.62°) and $\mathbf{T^1/T^2}$ (177.17°) indicate the flattened structure of the molecule (with the exception of the F and H atoms of the methyl groups).



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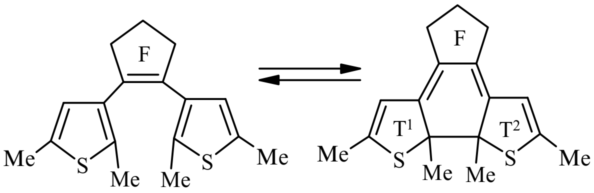

41 A **41 B**

In the planar fragment of the molecule, as in compound **11B**, it is possible to separate out a new plane for the system of conjugated bonds.

Interesting features of compounds **40** and **41** are that their monocrystals are capable of multiple photochromic transitions **A** ⟷ **B** without disturbing the crystal structure, and they are stable in the dark almost to 100°C. The spatial coincidence of the crystal structures of **41A** and **41B** shows that on **A** → **B** transition the thienyl fragments are unfolded by about 35° relative to ring **F** without disturbing the crystal. The mechanism of such a transition is as yet unexplained, but is probably linked with the specific packing of the molecules in the crystal. Nevertheless this circumstance is extremely important, since it offers the possibility of using monocrystals directly for optical storage and for erasing entries.

The X-ray crystallographic data for dithienylethenes have a practical value. Thus the open form **A** of diester **7** on UV irradiation in various solutions is cyclized into form **B** and correspondingly is opened on irradiation with visible light. However the initial form **A** is not transformed into form **B** on UV irradiation in the crystalline state. The X-ray structural data indicate that the reason for this is the unfavorable conformation which the molecules occupy on packing in the crystal. In the crystal the thiophene rings are disposed nominally in a *trans* conformation, in which the distance between positions 2 and 2' is much greater than the standard van der Waals contact and rotation around the C–C bond is difficult. On practical use of the photochromes, i.e. before preparing films from them, it is recommended to first irradiate solutions of them to transpose them into the cyclized form, and to prepare the films or mixtures in the absence of visible light. The X-ray structural data for the diheterylethylenes have also been considered in a review [68].

The energy characteristics, charges on atoms, and geometry of the series of photochromes mentioned in the present review, have been studied within the framework of the semiempirical quantum-chemical MNDO approach [69]. A series of studies is planned to link photochromic properties of compounds with their structure.

It is fully evident that due to their unique photochromic properties the dithienylethenes are widely used in practice. Even now when there is still no industrial manufacture of photochromes *Chemical Abstracts* has information on more than 150 patents linked with these compounds. Use in practice, naturally, requires the construction of products with a wide assortment of different physicochemical properties. The solution of this problem lies in various directions, but will definitely include the search for new bridge ethylenic fragments, the development of convenient methods of obtaining condensed heterocyclic compounds, and the creation of efficient approaches towards assembling these components into a single photochromic system. There is no doubt that these apparently exceptional problems in the chemistry of dithienylethenes will stimulate methods of heterocyclic synthesis, since the final aim, the construction of industrially available, thermally irreversible photochromes offers limitless opportunities.

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