Chemistry of Heterocyclic Compounds, Vol. 32, No. 6, 1996

POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.
14.* HALOCHROMISM OF POLYFURYL(ARYL)ALKANES

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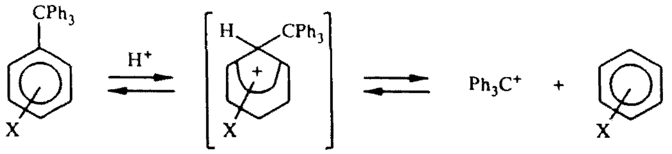
It was concluded on the basis of the similarity between the electronic spectra of difurylarylmethanes and trifurylalkanes and the spectra of the corresponding arylfurylcarbinols and difurylcarbenium perchlorates in concentrated sulfuric acid that the appearance of color in the solutions of polyfuryl(aryl)alkanes in concentrated sulfuric acid results from their disproportionation at the carbon—carbon bond with the elimination of the furan ring. The disproportionation of difurylalkanes, containing a methine hydrogen atom at the central carbon atom, under these conditions is accompanied by hydride transfer.

Halochromism or acidochromism (the appearance of color during the interaction of organic compounds with acids) has been known for a long time and has been studied mainly for the aromatic halogen derivatives of methane and arylcarbinols. The appearance of color during the dissolution of such compounds in acids is attributed to the formation of carbocations, as demonstrated by various methods [2]. In a series of cases, however, it was difficult to explain the mechanism of the appearance of color in the solutions. This applies, in particular, to the halochromism of the aromatic derivatives of alkanes. Papers by Lavrushin and coworkers [3-7] were devoted to the study of this problem. Using the obtained experimental data, the authors came to the conclusion that, as also in the case of carbinols, the appearance of color during the interaction of polyarylalkanes with acids is explained by the formation of carbenium ions. Investigation of the dependence of the rate of the reaction of tetraarylmethanes with acid on the acidity function H_0 [8] gave the authors reason to suppose that the cleavage of the derivatives of tetraarylmethanes takes place through a stage involving protonation of one of the benzene rings, followed by its elimination.



In spite of the large amount of published information on the halochromism of the aromatic derivatives of methanes, due attention has not been paid to study of this effect in the series of polyfuryl(aryl)alkanes, and this is probably due to the acidophobic nature of alkylfurans. However, according to existing data [9], the derivatives of furan are fairly stable in concentrated sulfuric acid at the concentrations used for spectroscopy. The spectra of 2,2-difurylpropane and *gem*-trifurylethane under these conditions were described in [10]. Such spectra have an absorption band in the long-wave region with a bathochromic shift, due to the number of furan rings in the molecule. Electronic spectra of alcohol solutions of such compounds are characterized by an absorption maximum at λ_{max} 220-230 nm, irrespective of the number of furan rings [11, 12].

More recently, a structure with a pentacoordinated carbon atom was proposed in order to interpret the data obtained during spectroscopic investigation of sulfuric acid solutions of di- and trifurylalkanes [13]. However, to explain the appearance of color in the acidic solutions of polyfuryl(aryl)alkanes there are, in our opinion, no reasons for using a mechanism other than

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*For Communication 13, see [1].

Kubansk State Technological University, Krasnodar. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 738-741, June, 1996. Original article submitted February 21, 1996.

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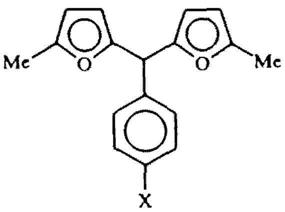
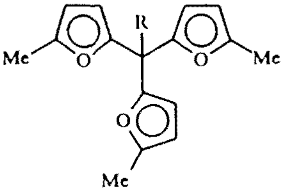
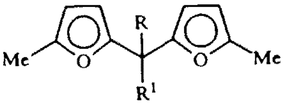
that proposed earlier for the aromatic analogs. The lability of the C—Fur bond in polyfuryl(aryl)alkanes has already been demonstrated in one of our previous communications [14].

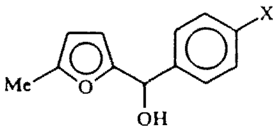
In the present paper, therefore, we will present data indicating that polyfurylalkanes are cleaved at the carbon—carbon bond linking the central "methane" carbon atom to one of the furan rings when they are dissolved in concentrated sulfuric acid.

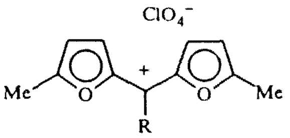
The electronic spectra of solutions of difurylarylmethanes (Ia-f), trifurylalkanes (IIa, b), and difurylalkanes (IIIa-c) in sulfuric acid are presented in Table 1. A characteristic feature of the spectra of compounds (Ia-f) and (IIa, b) is the presence of strong absorption ($\log \varepsilon = 3.62$-5.07) in the region of $\lambda_{max} = 400$-500 nm.


Ia-f


IIa, b

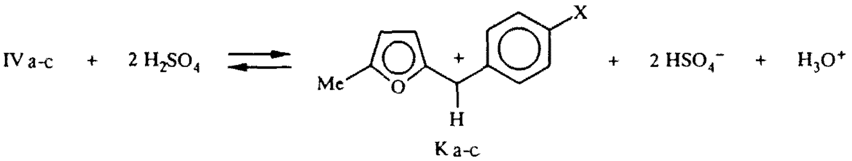

IIIa-c


IVa-c

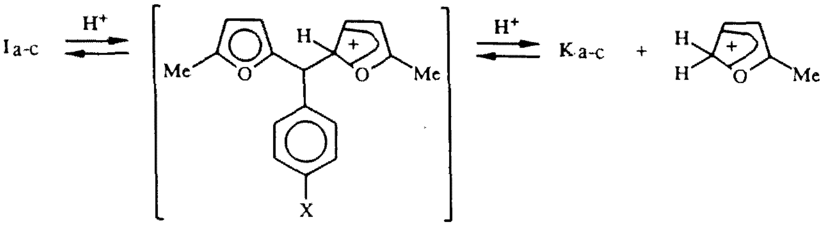

Va, b

I, IV a X - H; b X - Me; c X - OMe; I d X - OH; e X - Br; f X - NO_2; II a R - H; b R - Me;
III a R - R^1 - H; b R - H, R^1 - Me; c R - R^1 - Me

A similar type of light absorption is found during comparison of the electronic spectra of the difurylarylmethanes (Ia-c) with the spectra of the corresponding carbinols (IVa-c) (Table 1). It is known that arylcarbinols undergo reaction of the acid—base type with concentrated sulfuric acid, forming carbenium ions [2]. Thus, the formation of the corresponding carbocations Ka-c must be expected when furylarylcarbinols are dissolved in sulfuric acid.



The similarity of the spectra of compounds (Ia-c) and (IVa-c) makes it possible to suppose that the cations Ka-c are also formed in sulfuric acid solutions of difurylarylmethanes.



Evidence for the cleavage of the carbon—carbon bond in the trifurylalkanes (IIa, b) during the reaction with sulfuric acid is provided by the complete agreement of the λ_{max} values in the electronic spectra of compounds (IIa, b) and the perchlorates (Va, b) (Table 1).

During investigation of the spectra of the difurylalkanes (IIIa, b) we found that the absorption curves contain two maxima in the long-wave region at λ_{max} 334 and 315 nm for the first and 489 and 487 nm for the second. The last values coincide with λ_{max} in the spectra of the difurylmethyl (Va) and *gem*-difurylethyl (Vb) cations (Table 1, Fig. 1). The appearance of these absorption bands can be explained by the hydride transfer reaction, previously observed for the derivatives of tri- and diarylmethanes [6].

TABLE 1. Electronic Absorption Spectra of Compounds (Ia-f, IIa, b, IIIa-c, IVa-c, Va, b) in Concentrated Sulfuric Acid

Compound	λ_{max} (log ε)	Compound	λ_{max} (log ε)	Compound	λ_{max} (log ε)
Ia	438 (4,68)	IIa	489 (4,92)	IVb	460 (4,71)
Ib	459 (4,60)	IIb	487 (5,07)	IVc	495 (4,61)
Ic	491 (4,83)	IIIa	335 (3,62), 489 (3,91)	Va	489 (4,86)
Id	473 (4,71)	IIIb	315 (4,08), 487 (3,67)	Vb	487 (4,98)
Ie	459 (4,77)	IIIc	329 (4,47)		
If	405 (4,61)	IVa	439 (4,54)		

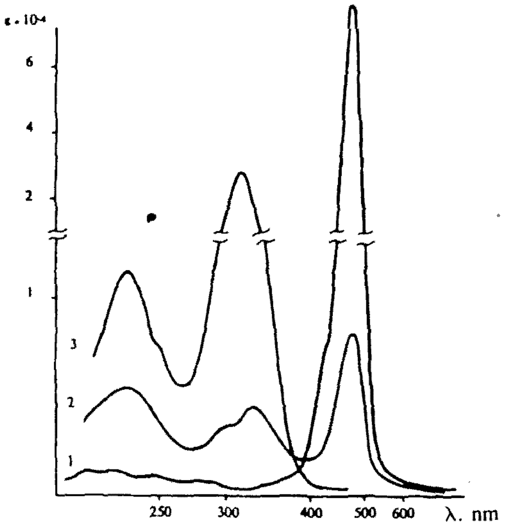
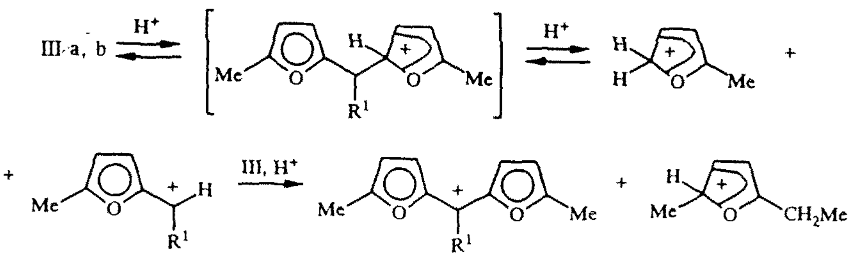


Fig. 1. Electronic spectra in concentrated sulfuric acid: 1) Bis(5-methyl-2-furyl)carbenium perchlorate; 2) bis(5-methyl-2-furyl)methane; 3) 2,2-bis(5-methyl-2-furyl)propane.



This is confirmed by the fact that the spectrum of 2,2-difurylpropane (IIIc), which cannot enter into hydride transfer, is characterized by only one strong absorption band with λ_{max} = 329 nm (Table 1, [10], Fig. 1).

The familiar release of phenol during the treatment of a sulfuric acid solution of 4-hydroxytriphenylmethane with a saturated solution of sodium acetate is important for confirming the mechanism proposed for the reaction of the aromatic derivatives of alkanes with acids [4]. The second product was 1,1-diphenylethane, which is formed as a result of the dehydration of diphenylmethylcarbinol.

Any attempts to isolate any products from the sulfuric acid solutions of polyfuryl(aryl)alkanes led to resinification of the reaction mass. In spite of this, however, in our opinion the presented experimental data confirm the proposed mechanism.

EXPERIMENTAL

The electronic spectra were obtained on a Specord M-40 instrument.

Compounds (Ia-f, IIa, IIIa-c) were obtained by the method in [11], compound (IIb) was obtained by the method in [15], compounds (IVa-c) were obtained by the method in [16], and compounds (Va, b) were obtained by the method in [17].

Preparation of Solutions. A 0.0035-0.0042-g sample of the substance was dissolved in glacial acetic acid in a 25-ml measuring flask, 0.8-1.2 ml of the solution was taken and diluted with concentrated sulfuric acid with cooling and vigorous stirring, and the total volume was made up to 25 ml.

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