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REGIOSELECTIVITY OF THE ALLYLATION OF BENZOTHIOPHENE

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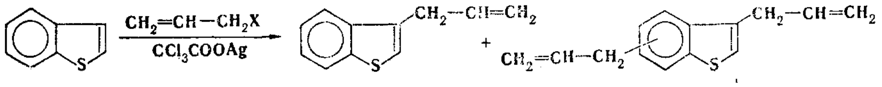
The reaction of benzothiophene with allyl halides in the presence of silver trichloroacetate in chlorine-containing hydrocarbons was investigated. It was established by gas–liquid chromatography and ^{13}C NMR and mass spectrometry that 3-allylbenzothiophene and diallylbenzothiophene are formed in this case. The ^{13}C NMR spectra were interpreted on the basis of an additive scheme with the utilization of benzothiophene, thiophene, and 2- and 3-allylthiophenes as models.

The known reactions involving the alkylation of benzothiophene have been carried out under acid catalysis conditions [1-3]. However, the possibility of migration of the alkyl group in this case [4] leads to a mixture of 2- and 3-alkylbenzothiophenes, i.e., it makes the reaction nonselective. We therefore set up experiments under conditions that exclude positional isomerization. These conditions are realized in the allylation of furan or benzofuran by allyl halides in the presence of silver trichloroacetate in chlorine-containing hydrocarbons [5, 6].

It was found that the allylation of benzothiophene with allyl iodide in the presence of silver trichloroacetate proceeds, according to the results of gas–liquid chromatography (GLC) and ^{13}C NMR spectroscopic and mass spectrometric data, to give only 3-allylbenzothiophene (I) when the experiment is carried out for less than 5 min (Table 1). This fact is in good agreement with the literature data on electrophilic substitution in benzothiophene, which takes place primarily in the 3 position. An increase in the reaction time leads to the appearance in the reaction mixture of another compound which, according to mass spectrometric data, has a molecular weight of 214, i.e., diallylbenzothiophene (II), in which the second allyl group is evidently located in the benzene ring. Replacement of allyl iodide by the corresponding bromide promotes an increase in the selectivity of the allylation of benzothiophene (Table 1).



I

II

X = Br, I

The assignment of the resonance signals in the ^{13}C NMR spectrum of I was made with the use of the additive principles of ^{13}C chemical shifts. We selected thiophene, 2-allylthiophene, and 3-allylthiophene as models for the construction of the additive scheme. The carbon magnetic resonance spectra of these compounds were analyzed on the basis of the literature data (for thiophene [7] and from the $^{13}C{-}^{1}H$ spin–spin coupling constants for alkylthiophenes [8]), the ^{13}C monoresonance spectra of 2-allyl- and 3-allylthiophenes, and by the use of 2-D- and 3-D-benzothiophenes as models. We carried out the assignment of the resonance signals of the 4-C and 7-C atoms of the six-membered ring of benzothiophene by the "fingerprint" method [9] and obtained results that are in agreement with the recently published results [10] on the basis of an analysis of a series of alkylbenzothiophenes (Table 2).

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TABLE 1. Results of Experiments on the Allylation of Benzothiophene (at 20°C for a benzothiophene—silver trichloroacetate—allyl iodide ratio of 2:1:1 and a benzothiophene concentration of 0.0056 mole/liter)

Solvent	Exptl. time, min	Yields of products of allylation of benzothiophene, %	
		3-allylbenzothiophene	diallylbenzothiophene
Acetonitrile	120	6	—
Nitromethane	120	25	19
Tetrachloroethane	120	34	20
1,2-Dichloroethane	5	21	—
The same	120	27	10
„ „	120	28	2*

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*The experiment was carried out with allyl bromide.

TABLE 2. ^{13}C Chemical Shifts (in parts per million relative to tetramethylsilane) of Model Compounds and Increments of Allyl Substitution in Thiophene

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Notes
Benzothiophene	125,61	123,34	123,14	123,61	123,69	121,96	139,25	139,43	a
	126,12	123,69	123,57	124,10	124,17	122,44	139,57	139,71	b
Thiophene	124,71	126,47	124,71						a
	125,4	127,2	127,2	125,4	—CH_2—	CH_2=	=CH–		c
2-Allylthiophene	142,09	123,14	126,36	124,22	33,89	115,82	136,13		a
	140,0	122,6	128,3	123,1					d
	(+17,4)	(–3,3)	(–0,1)	(–0,5)					e
3-Allylthiophene	120,39	139,72	127,72	124,97	34,36	115,41	136,50		a
	119,7	136,8	130,7	125,8					d
	(–4,3)	(+13,3)	(+1,3)	(+0,3)					e

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a) These are the chemical shifts recorded in the present research (±0.05 ppm); CCl_4 was used as the solvent in all cases. b) Data from [7]. c) Data from [9]. d) These are the chemical shifts (in parts per million) calculated with the aid of the increments of methyl substitution in cyclopentadiene [18]. e) These are the increments of the chemical shifts of the carbon atoms (in parts per million) in the case of allyl substitution in thiophene.

TABLE 3. Chemical Shifts of the Carbon Atoms of the Product of Monoallylation of Benzothiophene and Results of Calculation of the Shifts of the Carbon Atoms of 2- and 3-Allylbenzothiophenes via an Additive Scheme

Compound	C-2	C-3	C-4; C-7	C-5; C-6	C-8	C-9	CH_2=	–CH=	–CH_2–	Notes
Reaction product	121,68	135,35	121,49 121,30	122,45 123,44	138,57	140,45	116,22	135,18	32,65	a
3-Allylbenzothiophene	121,3	136,6			139,5	140,7				b
2-Allylbenzothiophene	143,0	120,0			139,3	138,7				b

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a) The ^{13}C chemical shifts were measured in parts per million relative to tetramethylsilane with an accuracy of ±0.05 ppm for a solution of the product of allylation of benzothiophene in CCl_4. b) The chemical shifts (in parts per million) were calculated on the basis of an additive scheme of the increments of allyl substitution in thiophene.

It is known that the effects of heteroorganic substitution on the chemical shifts of the carbon atoms of the cyclopentadienyl ring and the five-membered indene fragment coincide with an accuracy of 0.5 ppm [11]. A qualitative evaluation of the ^{13}C chemical shifts of allylthiophenes with the aid of increments of methyl substitution in cyclopentadiene gives good agreement with the experimental results (Table 2). This makes it possible to use the increments of the chemical shifts of the carbon atoms in allylthiophenes in the calculation of the ^{13}C shifts of five-membered 2- and 3-allylbenzothiophene fragments. Mutually unambiguous agreement between the calculated values and the experimental chemical shifts of the carbon atoms of the product of the allylation of benzothiophene is realized only for the 3-allylbenzothiophene structure.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded with Varian XL-100-15 and CFT-20 spectrometers under pulse conditions of rapid Fourier transformation with the use of ampules with diameters of 12 and 10 mm, respectively. Stabilization of the resonance conditions was realized by deuterated standards (d_6-benzene and d_{12}-cyclohexane) placed in the inner bushings with a diameter of 3-5 mm. Complete suppression of the $^{13}C-^{1}H$ spin—spin coupling was achieved on the basis of the method of "noise" modulation of the irradiating high-frequency field [12] with a noise bandwidth of 1000-2000 Hz during recording of the survey spectra. The ^{13}C monoresonance spectra were obtained under pulse double-resonance conditions [13].

A solution of allyl halide in dichloroethane was added slowly to a mixture of benzothiophene and silver trichloroacetate in dichloroethane. At the end of the reaction, the mixture was diluted with ether, and the precipitate was removed by filtration, washed with 10% sodium carbonate and water (until the water washings were neutral), dried with magnesium sulfate, and distilled. 3-Allylbenzothiophene with bp 132°C (7 mm) was isolated from the reaction products.

2-D-Benzothiophene. This compound was obtained in 50% yield by the addition of D_2O to an ether solution of 2-benzothienyllithium at —20°C. The product had bp 70°C (10 mm) and contained 98% deuterium (according to mass spectrometry).

3-D-Benzothiophene. This compound was obtained in 55% yield by the addition of D_2O to an ether solution of 3-benzothienyllithium at —70°C. The product had bp 70-71°C (10 mm) and contained 97% deuterium (according to mass spectrometry).

2-Allylthiophene. This compound, with bp 40-41°C (5 mm), was obtained in 41% yield by the reaction of 2-thienyllithium in ether with allyl bromide at —20°C.

3-Allylthiophene. This compound, with bp 45-46°C (9 mm), was similarly obtained in 31% yield from 3-thienyllithium at —70°C.

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