International Engineering Journal For Research & Development

Vol.6
Issue 4

NITRATION OF ACETYL-1-THIAINDANES AND 1-THIOCHROMANES

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ABSTRACT

This article is aimed at studying the electrophilic gap in the aromatic part of the molecule of benzothiophene and thiochroman derivatives with nitrating agents.

Keywords: Acetylthiochroman, nitrating mixture, electophile, deactivation, spectroscopy, electron donor, electron acceptor, nitro group.

INTRODUCTION

The electrophilic substitution of benzothiophene derivatives was initiated, first of all, with the reaction with nitrating agents. The nitration of 1-thiaindane and its homologues was studied by Karimov, Nasyrov and Numanov under the conditions of the action of acetyl nitrate at 30-40 ° C in a solution of carbon tetrachloride. At the same time, they managed to get mainly mononitro-industrial ones with a yield of up to 80%. When 1-thiaindans are acted upon with dilute nitric acid, as it turned out, a mixture of mono-, di- and trinitro-producing ones is formed, the use of a mixture of nitric and acetic acids makes it possible to obtain 1-thiaindans with one nitro group, but the yield is only 40-45% and the location of the nitro groups is uncertain ... [1; 12-19 s]

MATERIALS AND METHODS

Synthesis of 7-nitro-5-acetyl-2-methyl-1-thiaindane

In a two-necked flask equipped with a mechanical stirrer and a dropping funnel, 2 g (0.01 mol) of 5-acetyl-2-methyl-1-thiaindane was dissolved in 5 ml of sulfuric acid. The resulting solution is cooled to 0 ° C and within 10 minutes while the stirrer is running, 10 ml of a nitrating mixture is added dropwise from a dropping funnel. Stirring is finished 30 minutes after the addition of the nitrating mixture. Then, stirring the contents of the flask, pour into a glass with 25 ml of water and pieces of ice. An hour later, it was filtered off, washed with water, dried in air and crushed. The yield is 2 g (83%). Melting point 165-166 ° C.

Synthesis of 8-nitro-6-acetyl-1-thiochroman

The reaction was carried out similarly to the synthesis of 7-nitro-5-acetyl-2-methyl-1-thiaindane. Was taken 2 g (0.01 mol) of 6-acetyl-1-thiochroman. The yield is 2.1 g (85%). Melting point 153-154 0C.

Synthesis of 8-nitro-6-propionyl-1-thiochroman

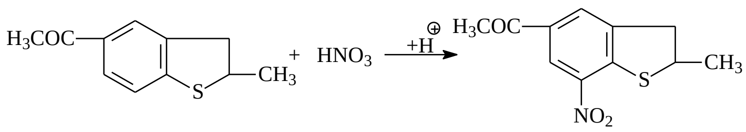
The reaction was carried out similarly to the synthesis of 7-nitro-5-acetyl-2-methyl-1-thiaindane. Was taken 2 g (0.01 mol) of 6-propionyl-1-thiochroman. Yield 1.45 g, (63%). Melting point 161-162 ° C.

RESULTS

This work proposes the study of the chemical properties of acetylthiaindanes and acylthiochromanes in reactions with nitrating agents. It is known that the deactivating effect of the carbonyl group on the aromatic ring hinders electrophilic substitution, and in the absence of additional activating substituents, the reaction proceeds only under severe conditions.

The molecules of 5-acitel-2-methyl-1-thiaindane, 6-acetyl-1-thiochroman, and 6-propionyl-1-thiochroman were subjected to nitration reactions. The experiments were carried out in an environment of sulfuric acid at a temperature of 00C for 30 minutes. To introduce a nitro group into the aromatic nucleus of acyl derivatives of 1-

thiaindanes and 1-thiochromanes, we chose as a nitrating agent a mixture of equal volumes of concentrated nitric acid and sulfuric acid. The results of the reaction showed that the calculated amounts of concentrated nitric and sulfuric acid give good yields of mononitro derivatives of acetyl-1-thiaindanes and acetyl-1-thiochromanes:



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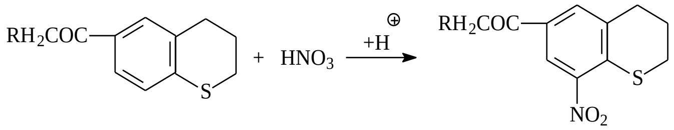

II. R= H; III. R=CH_3.

The location of the nitro group is assumed to be in the seventh position in acetyl-1-thiaindane molecules, and in the eighth position in acetyl derivatives of 1-thiochromanes, the aromatic part of the molecule.

The presence of a nitro group in the molecules of the synthesized mononitro derivatives of acetyl-1-thiaindanes and acetyl-1-thiochromanes was determined by IR and PMR spectroscopy and elemental analysis. In the PMR spectra of mononitro derivatives of acetyl-1-thiaindane and acyl-1-thiachromanes were compared with the spectra of the starting compounds. The signals of the protons of the acyl group and the saturated rings remain practically unchanged. This can be observed in the spectrum of the resulting compound, i.e., in the molecules of 8-nitro-6-acetyl-1-thichroman. In the 1 , 89 ppm, and 2.24 ppm. Spin-spin coupling constant CH2 (6 proton) = 7 Hz. The observation of the PMR spectra of mononitro derivatives has led to the fact that two strong electron-withdrawing groups at the aromatic part of the molecule, most likely, screen the appearance of signals of aromatic protons. The proton, which is located between two electron-withdrawing groups, is especially strongly screened. Therefore, no clear separation of signals from the aromatic part of the molecule is observed in the spectra of mononitro derivatives.

In the IR spectra of I, II, and III, the appearance of intense absorption bands in the region of 1700 cm-1 is attributed to the stretching vibrations of the carbonyl bond of the acyl group. The absorption band at 1620 cm-1 belongs to the stretching vibrations of the double bond in the benzene ring, and the absorption band at 840 cm-1 and 1180 cm-1 can be attributed to the stretching vibrations of CH in the benzene ring. The absorption bands at 1435 and 1475 cm-1 are characterized by the appearance of the CH3 group, and the absorption band in the region of 2940 cm-1 can be attributed to the stretching vibrations of the CH2 group. The absorption band in the region of 1550 cm-1 confirms the presence of a bond of the Ar-NO2 group, and the absorption band in the region of 755 cm-1 can be attributed to the stretching vibrations of the C-S-C bonds.

The yields, physicochemical characteristics, and elemental analysis data are shown in Table 1. Typical absorption bands of nitroproducts acetyl-1-thiaindane and acyl-1-thiachromanes are shown in table 2.

Physicochemical constants mononitro derivatives acyl-1-thiaindanes and acyl-1-thiachromanes

Table 1

№ Conn.	The names of the compounds.	Output %	Mp ° C.	Found,%.		Gross formula	Calculated,%.	
				C	H		C	H
I	5-Acetyl-2-methyl-7-nitro-1-thiaindane	83	165-166	55,78 55,73	4,78 4,74	$C_{11}H_{11}O_3SN$	55,61	4,67
II	6-Acetyl-8-nitro-1-thiochroman	85	153-154	55,73 55,68	4,90 4,75	$C_{11}H_{11}O_3SN$	55,61	4,67
III	6-Propionyl-8-nitro-1-thiochroman	65	161-162	57,70 57,61	5,43 5,36	$C_{12}H_{13}O_3SN$	57,42	5,21

Characteristic absorption bands of mononitro derivatives acyl-1-thiaindanes and acyl-1-thiachromanes

table 2

Frequency assignment, cm-1	Compound		
	I	II	III
C = C in the benzene ring	1620	1620	1630
CH in the benzene ring	840	850	840
H in the benzene ring	1180	1140	1150
C-S-C	760	760	755
$Ar\text{-}NO_2$	1550	1575	1550

Currently, quantum chemistry is successfully solving many scientific problems. It is used to study the structure of matter, information on the densities of electronic states, the distribution of electron density, potential reaction surfaces and rearrangement barriers, investigate the mechanisms of chemical reactions, the calculation of various spectroscopic quantities, such as vibrational spectra, electronic and X-ray spectra, optical spectra, spectral parameters nuclear and electronic magnetic resonance. The results of molecular dynamics modeling presented in this article were obtained using the version of HyperChem 7.0 in the semiempirical approximation PM-3 [2; 28-32., 3; 247-253 s].

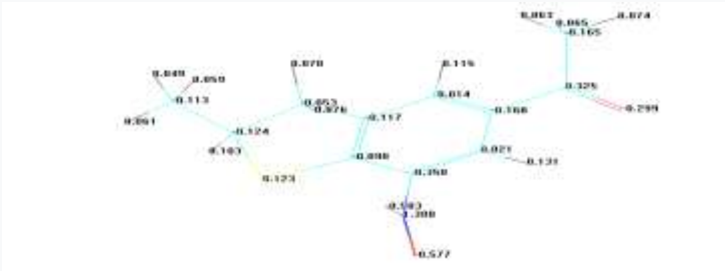

Figure 1. Distribution of effective charges on 5-acetyl-2-methyl-7-nitrothiaindane atoms

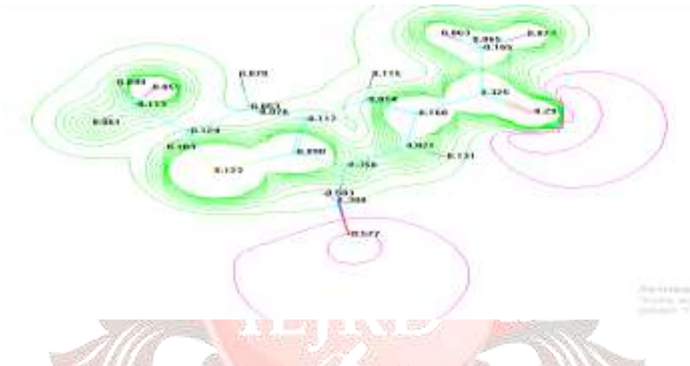

Figure 2. Electrostatic potential of a molecule 5-acetyl-2-methyl-7-nitrothiaindane

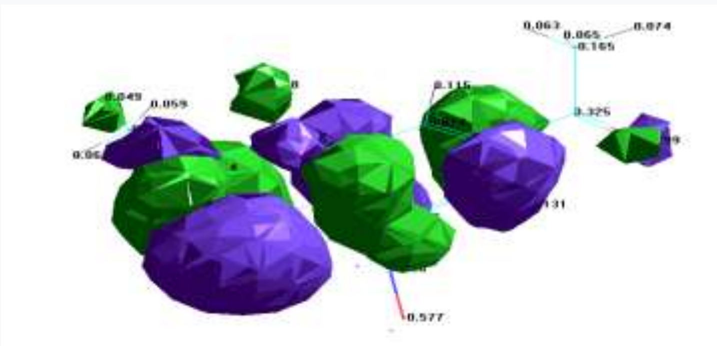

Figure 3. Molecular Orbital – HOMO

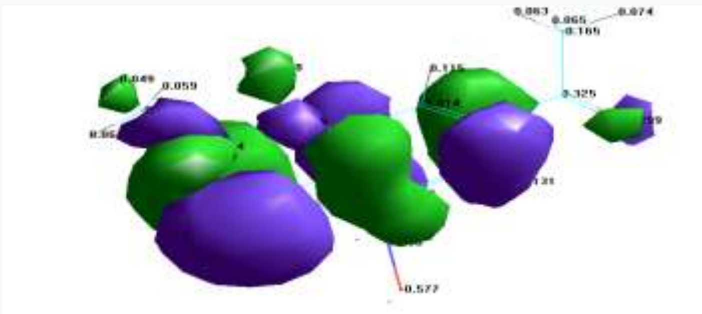

Figure 4. Molecular orbital – LUMO

Figures 3 and 4 show the molecular orbitals of HOMO and LUMO for the 5-acetyl-2-methyl-7-nitrothiaindane molecule. It should be noted that when considering the energy of atomic orbitals, the most important are the upper occupied molecular orbital (B3MO) and the lowest vacant (free) molecular orbital (LUMO or LUMO). B3MO characterizes the electron-donating properties of the molecule, and the B3MO energy is the ionization potential. LUMO characterizes the electron-acceptor properties of a molecule and the LUMO energy is the electron affinity energy. Thus, the higher the energy of the HOMO of organic molecules, the easier it is to donate electrons, and the lower the energy of the HOMO of molecules of organic substances, the easier they accept electrons. Other important calculated electronic characteristics are the Mulliken effective charges on atoms (CHARGES) and the system energy. The total energy value is the sum of the electron energy and the repulsive energy of the cores. The calculated energy parameters, which make it possible to judge the stability of the molecules, are given in Table 3.

Calculated energy parameters of a molecule

5-acetyl-2-methyl-7-nitrothiaindane according to the PM-3 method

Table 3.

Compound	E.tot., Kcal / mol	Effective charges on atoms, eV				
		(C=C)	(C=O)	(C-S)	(C-N)	(N=O), (N-O)
5-acetyl-2-methyl-7-nit-rotiaindane	-62250,29316	-0,117 -0,099	-0,2990	-0,123	1,308	-0,577; -0,583

Comparison of the values of effective charges on atoms in the molecules of the studied compounds showed that the most negative values are characterized by oxygen and nitrogen atoms in the descending order N-O → N = O → C = O → C-S → C = C → C-N. Due to the fact that there are many functional groups in the molecules of the studied compounds and the electronic potential is distributed throughout the molecule.

Thus, it can be concluded that semi-aromatic bicyclic sulfur-containing compounds behave like aromatic compounds in electrophilic substitution reactions in the aromatic part of the molecule.

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