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Nucleophilic Substitution Reactions of Some Tetrahalogeno Benzenes. Part I*

Reactions with oxygen and sulphur nucleophiles**

by

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Nucleophilic Substitution Reactions of Some Tetrahalogeno Benzenes. Part I[*]

Reactions with oxygen and sulphur nucleophiles[**]

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Reactions of some 1,2,3,5-tetrahalogen benzenes with sodium methoxide, sodium thioethoxide and sodium thiophenoxide were studied. Substrates were prepared with a new method in good yields. Reactions were succeeded only with pyridine, among several solvents and 2, 3, 5-trihalogenoanisoles with methoxide, 2,3,5-trihalogen thiophenetoles and 2,6-dithioethoxy-1,4-dihalogen benzenes with thioethoxide and 2,3,5-trihalogenodiphenyl thioethers and 2,6-Dithiophenoxy-1,4-dihalogeno benzenes were formad as reaction products. Structures of compounds were eluciadted by their IR and NMR spectra.

INTRODUCTION

Aromatic substitution reactions can be outlined in two main groups; a) Electrophilic substitution reactions, b) Nucleophilic substitution reactions. Formally nucleophilic substitution at aromatic carbon, seems like other nucleophilic substitutions.

$$\ddot{Y} + Ar \,\vdots\, - X \longrightarrow Y - Ar + \ddot{X}$$

This equation is the general scheme of aromatic SN reactions. A new bond at the reaction centre is formed by a rengent Y and the leaving group X is displaces together with its bonding electrons. Thus, in the course of reaction Y becomes more positive and X becomes more negative.

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The mechanisms of aromatic SN reactions were videly investigated and reviewed by a lot of authors (1, 2, 3).

Nucleophilic substitution reactions of simple Ar-X compounds such as halogeno-benzenes and- toluenes require drastic conditions while SN reactions of alkyl halides form in mild conditions.

In this work we studied the nucleophilic substitution reactions of some 1, 2, 3, 5-tetrahalogeno benzenes.

There are few records in the literature about 1, 2, 3, 5-Tetrahalogeno benzenes and they are generally about their preparations and physical properties. Among these, J. Burdon and his friends' works on tetrafluoro benzenes are related to our investigation (4, 5, 6, 7). Other works by Th. De Crauw (8) and by Bunnet and Victor (9) are on rucleophilic subsiution reactions of 1, 2, 3, 4-and 1, 2, 3, 5-tetrachloro benzenes and base catalyzed dehalogenation of 2, 4, 6-trichlorobromo benzene and 1, 2, 3, 5-tetrabromo benzene respectively. Anothers have studied the Jacobsen reaction of 1, 2, 3, 5-tetrabromo and tetraiodo benzenes (10).

EXPERIMENTAL SECTION

A) Preparation of Substrates and Primary Experiments.

The substrates we worked on were 1-Chloro (or bromo or iodo) 2, 4, 6-trichloro-, 1-Chloro (or bromo or iodo)- 2, 4, 6-tribromo- and 1-chloro (or bromo or iodo)- 2, 4, 6-triiodo benzenes. They were prepared from 2, 4, 6-trichloro, tribromo and triiodo anilines according to the methods given in the literature (11, 12, 13). Many of the substrates were also prepared according to Tüzün and Erk (14) in better yields.

Nucleophilic substitution experiments of the substrates were carried on with oxygen and sulphur nucleophiles such as methoxide, ethoxide, phenoxide, thioethoxide and thiophenoxide. Con centrated solutions Containing of excess of these nucleophiles were refluxed with substrates in methanol, ethanol, acetone, nitrobenzene, DMSO, etc. for 24–72 hours. These experiments failed and generally only the substrates were recovered at the end.

Experiments with methoxide, thioethoxide and thiophenoxide using pyridine as solvent were succesfull and 2, 3, 5-trihalogeno anisoles, 2, 3, 5-trihalogeno thiophenetoles, 2, 6-dithioethoxy-1,4-dihalogeno benzenes, 2, 3, 5-trihologeno diphenyl thioethers and 2,6-dithiophenoxy-1,4-dihologeno benzenes were obtained.

Structures of the products were elucidated from their IR and NMR spectra.

B) Synthesis of the Products.

1. Anisoles

In a 100 ml flat bottom flask 20 ml methanol and 1,15 g (0.05 mole) sodium was introduced. When sodium was disappeared excess of methanol distilled off under vacuum. Sodium methoxide left as a white, fine powder in the flask. The flask was cooled to the room temperature and a solution of 0,1 mole of 1, 2, 3, 5-tetrahalogeno benzen in 25 ml pyridine was added to the flask. The reaction mixture was refluxed about 15–16 hours. After cooling to the room temperature, the reaction mixture was poured into 150 ml of cold water with continious stirring. The crude product was separated as amorphous solid. 2, 3, 5-trihalogenoanisoles were crystallized from ethanol or methanol as colorless needles.

2. Thiophenetoles.

In a 100 ml flat bottom flask 6, 2 g (0,1 mole, 7, 3 ml) thioethanol and 25 ml Pyridine was introduced. A solution of 2 g (0.05 mole) sodium hydroxide in 10 ml of water was added to the flask with continious stirring. Lastly 0,01 mole of 1, 2, 3, 5-tetrahalogeno benzene in 15 ml pyridine was added and having equipped with a reflux condenser the reaction mixture was heated to 60–70 °C for 15 hours. At the end of the reaction 50 ml of water was added and the mixture transfered to a separatory funnel. The mixture was extracted with 40 ml. of ether and the etheral layer was shaken twice with dilute sodium hydroxide solution. Etheral solution was dried on Calcium chloride and ether and pyridine (under vacuum) was distilled. Remaining oil was dissolved in chloroform and apllied to an acidic aluminium oxide column. The first fraction was collected and crystallized from ethanol-water mixture with difficulty.

3. Dıphenyl thioethers.

The procedure is almost the same with described for thiophenetoles. In preparation of sodium thiophenoxide, metallic sodium mö and sodium amide suspention in toluene gave also satisfacto results.

RESULTS AND DISCUSSION

The compounds synthetized with sodium methoxide are listed in Table I. Reactions with some substrates didn't work. In some cases anisoles formed but could not be isolated. Their presence could be detected from the NMR spectrums of mixtures (e.g. 2-iodo-3,5-dibromo anisole from 1-iodo-2,4,6-tribromobenzene as shown in spectrum 3).

Table: I.

Substrate	Product	m.p. (*C)	Yield %	Spectrum No.
1,2,3,5-Tetrachloro benzene	2,3,5-Trichloro anisole	84	60	1.2
1-Bromo-2,4,6-Trichloro benzene	2-Bromo-3,5-dioloro anisole	92	53	
1-Chloro-2,4,6-Tribromo benzene	2-Chloro-3,5-dibromo anisole	102	70	
1,2,3,5-Tetra bromo benzene	2,3,5-Tribromoanisole	123–124	20	

As shown in Table II, two mono substituted and two disubstituted Products were obtanied from 1-chloro (and bromo)-2,4,6-trichloro benzenes and 1-chloro (and bromo)-2,4,6-tribromo benzenes respectively in reactions with sodium thioethoxide.

Tablo: II

Substrate	Product	m.p. (*C)	Yield %	Spectrum No.
1,2,3,5-Tetracholor benzene	2,3,5-Trichloro phenetole	46	33	4.5
1-Bromo-2,4,6-trichloro benzene	2-Bromo-3,5-dichlorophenetole	32	1	
1-Chloro-2,4,6-Tribromo benzene	2,6-Dithloethoxy-4-bromochlor bromochlor benzene	73	24.6	6.7
1,2,3,5-Tetrabromo benzene	2,6-Dithioethoxy-1,4-dibromo benzene	76	21	

These Products could be obtained from the reactions of sodium thiophenoxide. They are listed in Table III.

Table: III

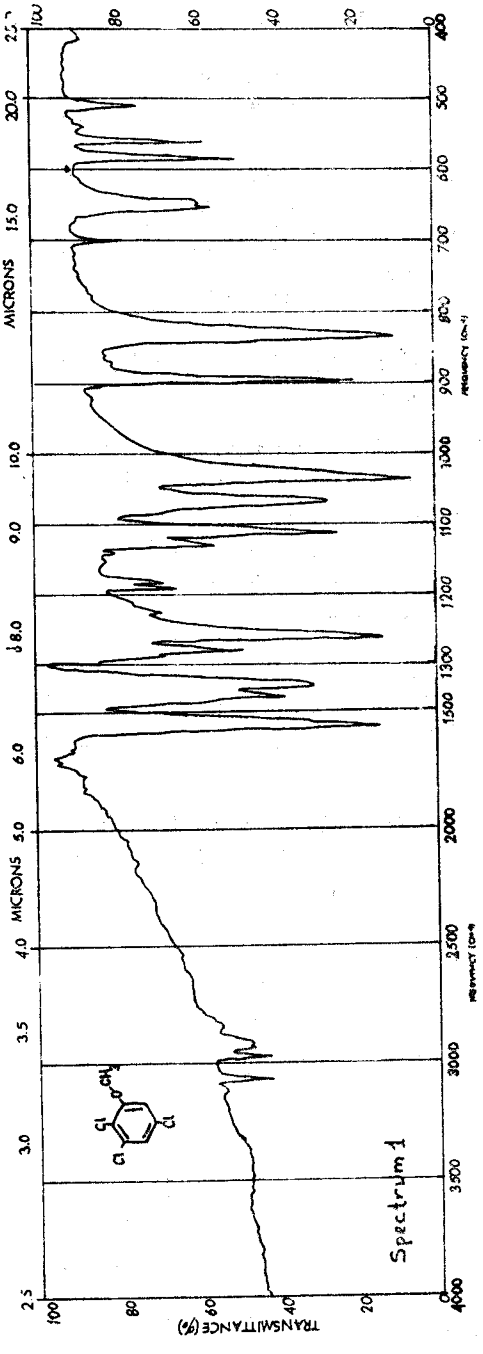
Substrate	Product	m.p. (*C)	Yield %	Spectrum No.
1,2,3,5-Tetrachloro benzene	2,3,5-Trichloro diphenyl thioether	81–83	55.3	8.9
1-Chloro-2,4,6-tribromo benzene	2,6-Dithiophenoxy-4-bromo chlor benzene	110–114	83.3	
1,2,3,5-Tetrabromo benzene	2,6-Dithiophenoxy-1,4-dibromo benzene	133	84.8	10.11

Satisfactory elemental analysis results were obtained for all products listed above.

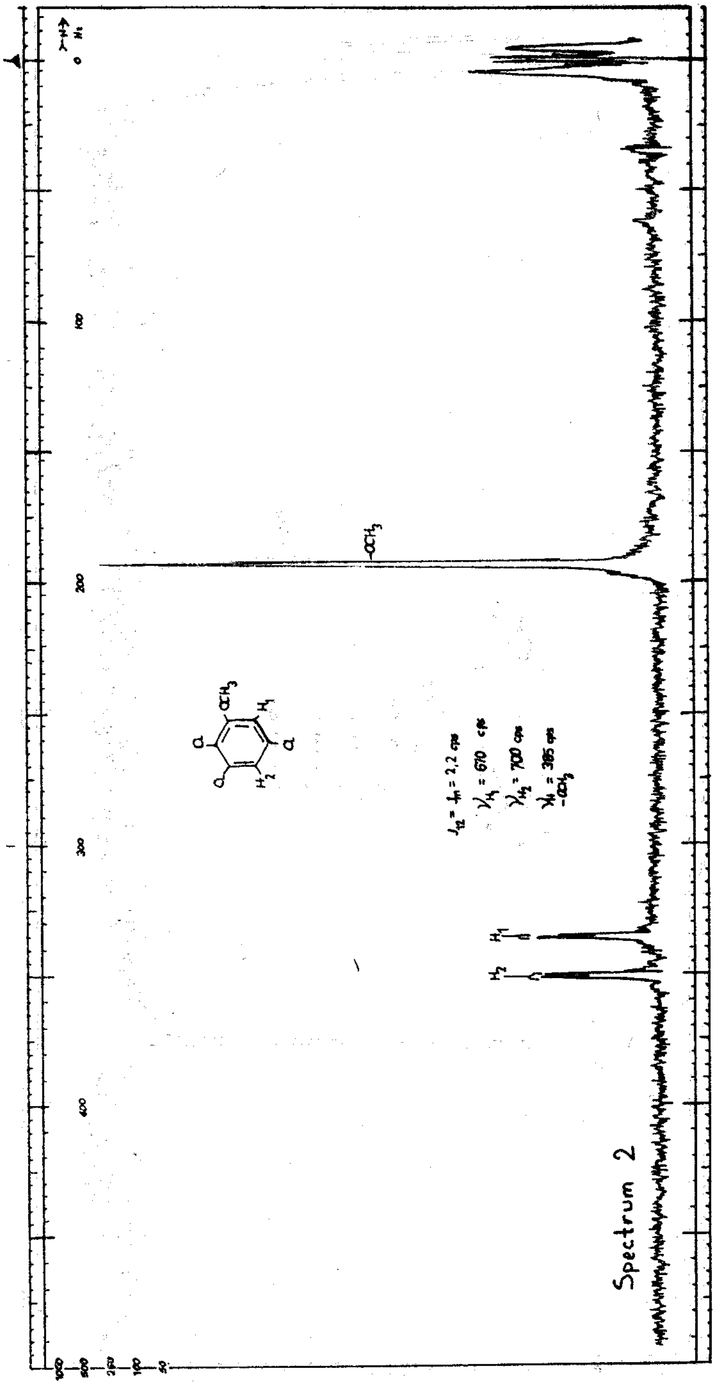
1-Iodo-2,4,6-trichloro benzene and 1-iodo-2,4,6-tribromobenzene behaved differently from other substrates in their series. They react partially or did not react with all three reactives. This Shows appreciable ortho-substituent effect of iodine. 1-Chloro (or bromo or iodo) -2,4,6-Triiodo benzenes didn't give any products at all. Substrates recovered in their reactions.

Our works are gave the same answer with Burdans works (4, 5, 6, 7) from the mechanistical point of view. Particularly, compounds occured by double substitution strictly confirms this suggest.

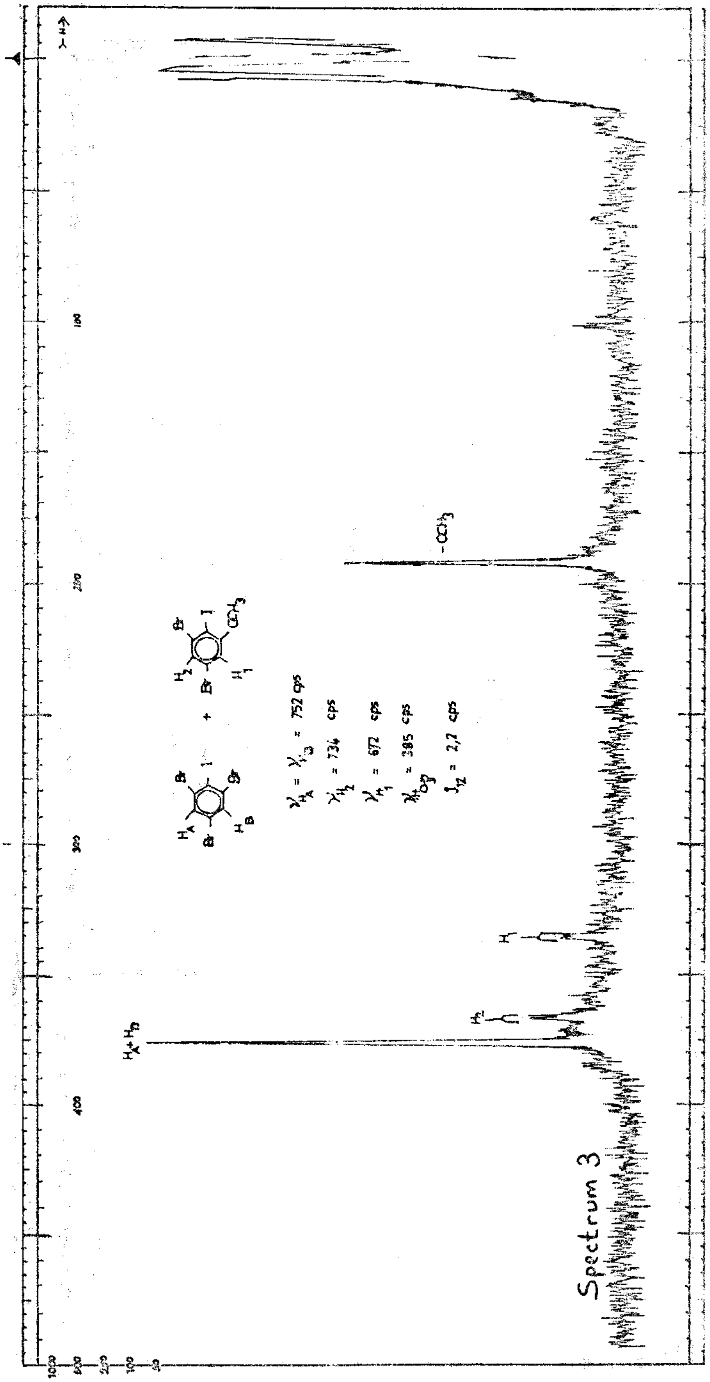
Pyridine as solvent has remarkable effect on reaction rates. This effeet is because of its basic chracter. It must be increasing the nucleophilic power of reactives.


2.5
3.0
3.5
4.0
MICRONS
5.0
6.0
8.0
9.0
10.0
MICRONS
15.0
20.0
25
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
FREQUENCY (CM-1)
2000
1500
1300
1200
1100
1000
900
FREQUENCY (CM-1)
800
700
600
500
400
Cl
Cl
Cl
O
CH3

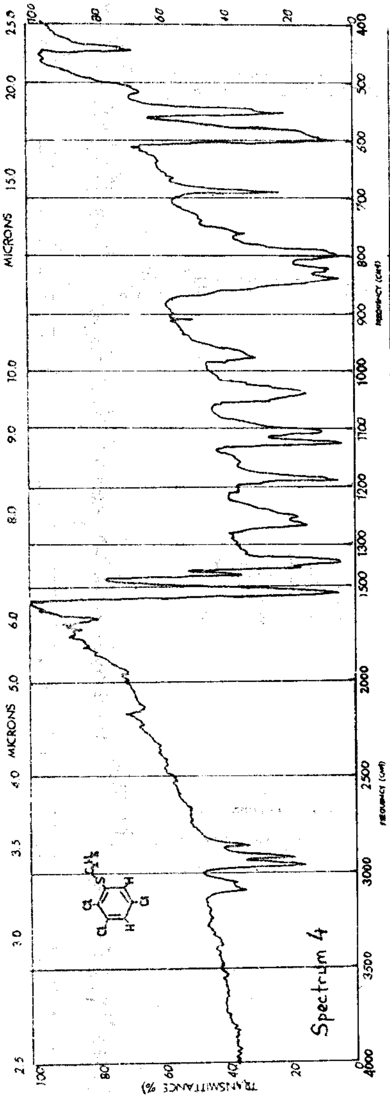
Spectrum 1


0
100
200
300
400
1000
500
250
100
50
-OCH3
H1
H2
Cl
Cl
Cl
OCH3
$J_{12} = J_m = 2,2$ cps
$\nu_{H_1} = 670$ cps
$\nu_{H_2} = 700$ cps
$\nu_{H\text{-}OCH_3} = 385$ cps

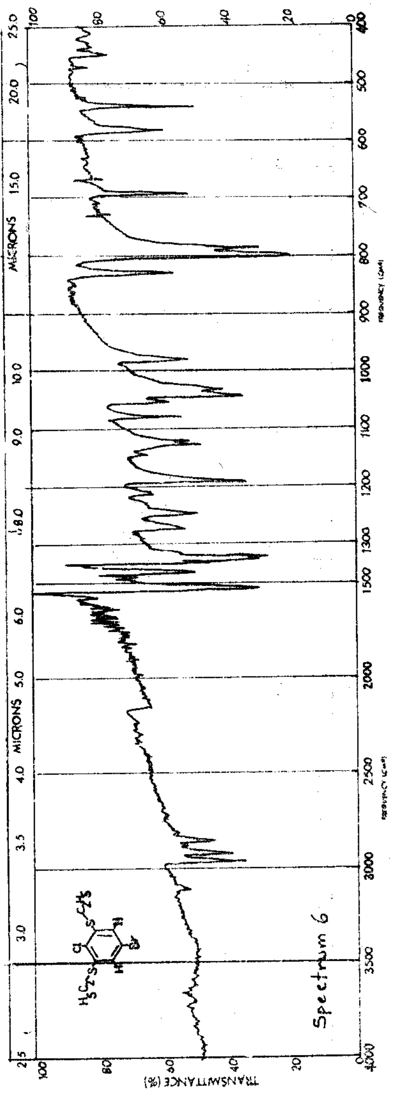
Spectrum 2


Br
H_A
Br
H_B
Br
I
+
H_2
Br
H_1
Br
I
CCH_3
ν_{H_A} = ν_{H_B} = 752 cps
ν_{H_2} = 734 cps
ν_{H_1} = 672 cps
ν_{CH_3} = 385 cps
J_{12} = 2,2 cps
-CCH_3
H_1
H_2
H_A+H_B
100
200
300
400
1000
500
250
100
50

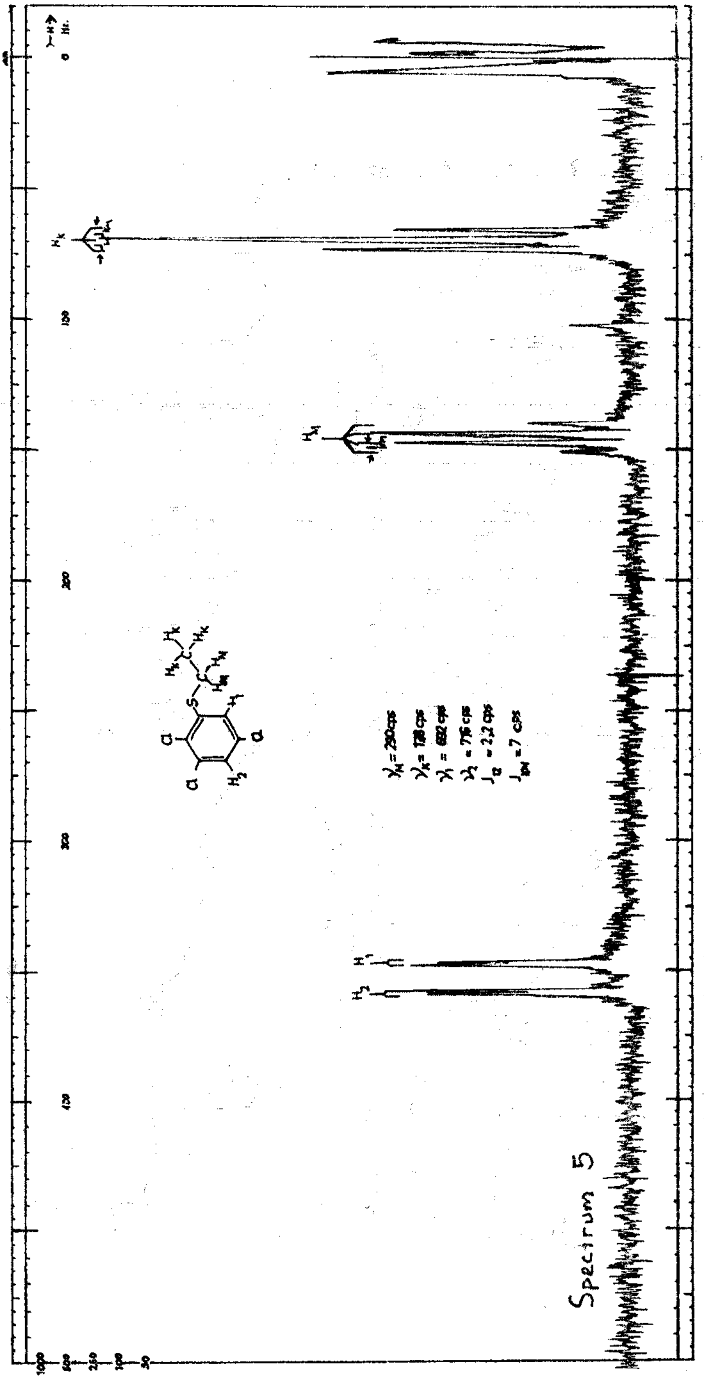
Spectrum 3

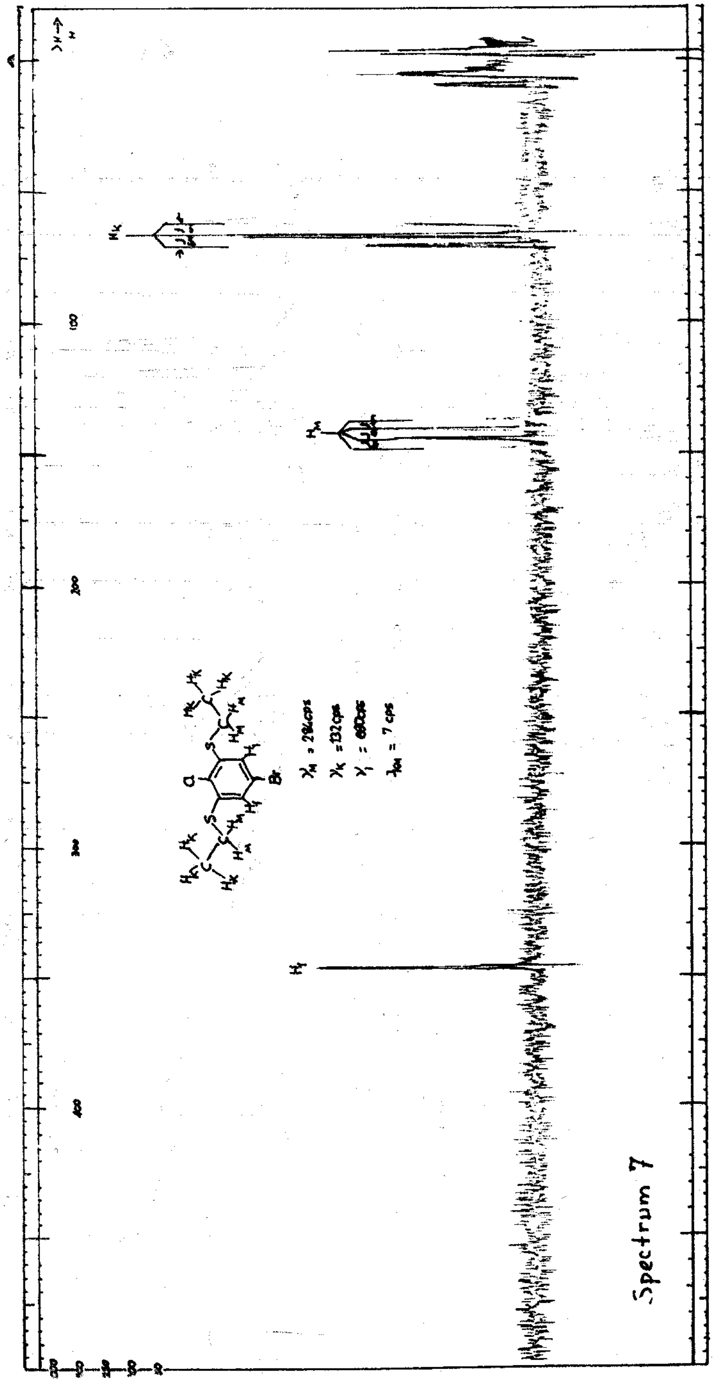


Spectrum 4



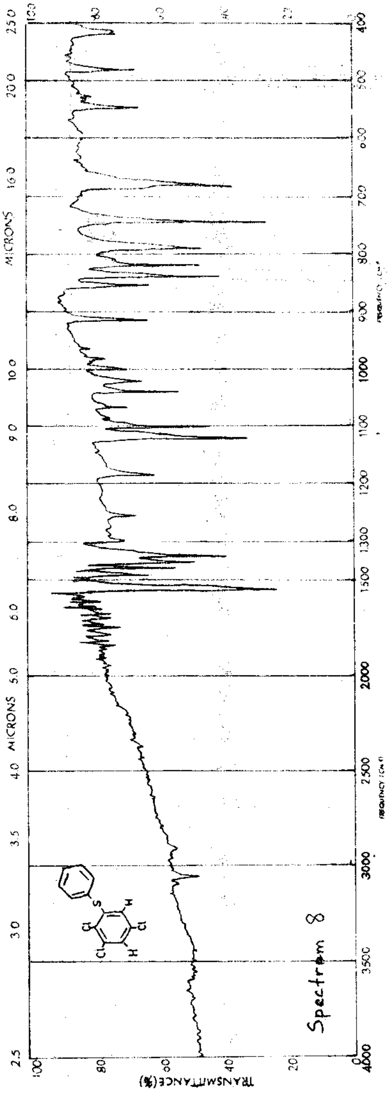
Spectrum 6


0 Hz.
100
200
300
400
1000
500
250
100
50
H_K
H_M
H_1
H_2
Cl
Cl
Cl
S
C
ν_M = 230 cps
ν_K = 178 cps
ν_1 = 682 cps
ν_2 = 716 cps
J_α = 2,2 cps
J_{KM} = 7 cps
Spectrum 5

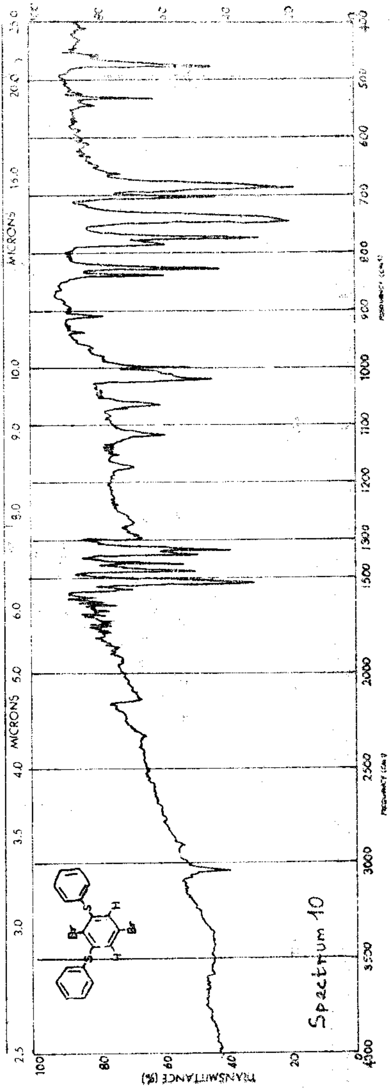


H_K
H_M
H_1
100
200
300
400
Cl
Br
S
ν_M = 284 cps
ν_K = 132 cps
ν_1 = 680 cps
J_{KM} = 7 cps

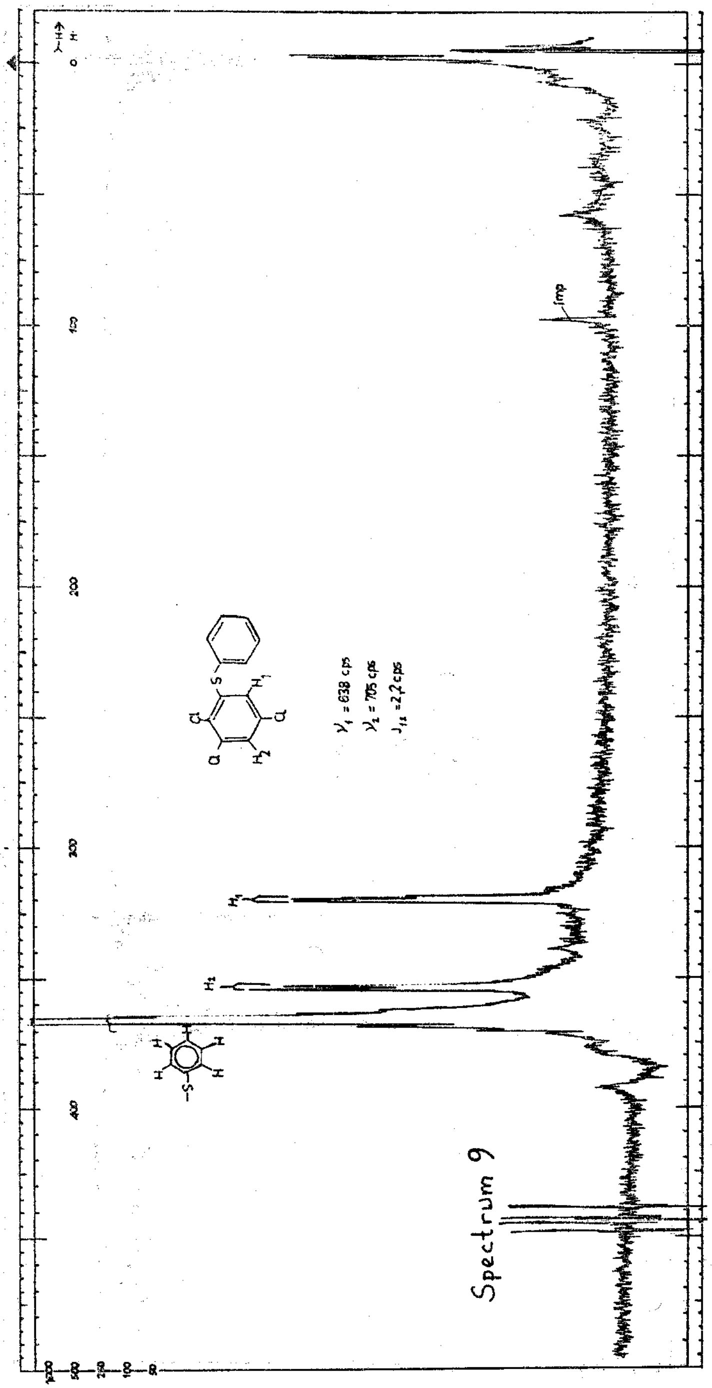
Spectrum 7



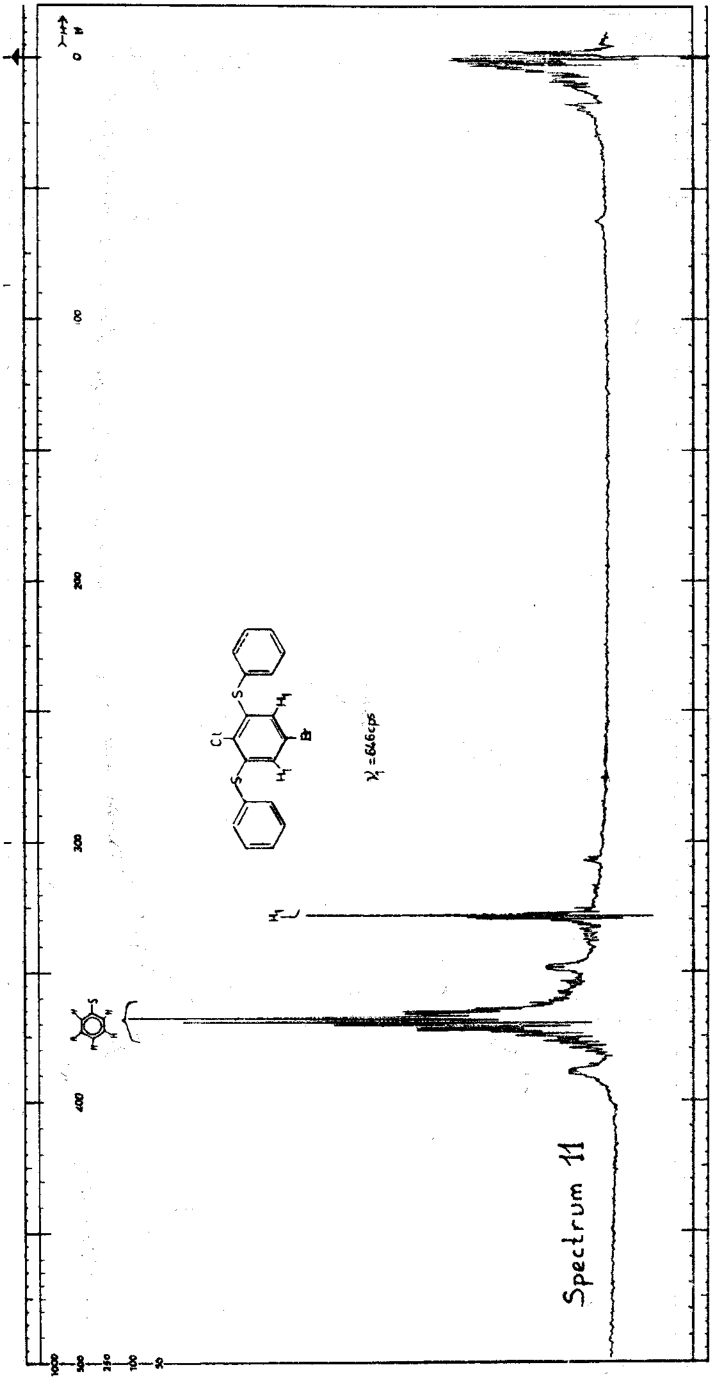
Spectrum 8



Spectrum 10


0
100
200
300
400
H₁
H₂
Imp
Cl
S
ν_1 = 638 cps
ν_2 = 705 cps
J_{12} = 2,2 cps
1000
500
250
100
50

Spectrum 9



Spectrum 11

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ÖZET

Bu çalışmada bazı 1,2,3,5-Tetrahalojen benzenlerin, metoksit, tiyoetoksit ve tiyofenoksit nükleofilleriyle sübstitüsyon reaksiyonları koşulları araştırılmıştır. Saptanan koşullarda reaksiyon ürünleri olarak sübstitüe anisoller, sübstitüe tiyofenoller ve sübstitüe difeniltiyo eterler sentezlenmiştir. Ürünlerin yapıları IR ve NMR spektrumları yardımıyla saptanmıştır.

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