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by

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Nucleophilic Substitution Reactions of Some Tetrahalogeno Benzenes. Part II*

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The reactions of some 1,2,3,5-tetrahalogeno benzenes with sodium piperidide and sodium pyrrolidide were studied. Free amines of reagents were used as solvents. The following products were obtained: with sodium piperidide, 2,6-dipiperidino-1,4-dihalogeno benzenes with sodium pyrrolidide, 2,6-dipyrrolidino-1,4-dibromobenzene and 2,4,6-tripyrrolidino chlorobenzene. An unexpected product from 1-iodo-2,4,6-tribromobenzene, namely 1,3-dipyrrolidino benzene was also formed in good yield. Structures of the products were elucidated from their IR and NMR spectra.

INTRODUCTION

Aromatic nucleophilic substitution has been introduced previously (1) but, as was mentioned, nucleophilic substitution reactions of 1, 2, 3, 5-tetrahalogeno benzenes have not been studied. We have therefore extended our work with nitrogen nucleophiles using amines which were known to be powerful nucleophiles.

EXPERIMENTAL SECTION

The substrates studied 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 of iodo)-2, 4, 6-triiodo benzenes. These were prepared fromo 2, 4, 6-trichloro tribromo and triiodo anilines according to the methods given in the literatüre (2, 3, 4), Many of the substrates were also prepared in better yields by the procedure of Tüzün and Erk (5).

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In nucleophilic substitution experiments with nitrogen nucleophiles, diethylamine, dipropylamine, diisopropylamine, morpholine, pyrrole, pyrrolidine and piperidine were tested. In these experiments amines themselves were used as reaction media. These experiments failed. The sodium salts of piperidine and pyrrolidine could be prepared with sodium amide and reactions of these derivatives were succesful. Products were obtained by the following procedures:

a) Dipiperidino benzenes.

10 g of sodium amide- in the form of a 50 % supension in toluene-were introduced into a 100 ml twin necked, flat bottomed flask; histot 25 ml of piperidine (freeshly refluxed and distilled over sodium) were added and the mixture was refluxed for 20–30 minutes, care being taken to exclude moisture. After slight cooling, 0,01 mole of 1, 2, 3, 5-tetrahalogeno benzene dissolved in 10 ml of piperidine were added through a dropping funnel. The reaction mixture was further refluxed for 20 hours and cooled to the room temperature. 25–30 ml of water was added carefully and the aqueous layer was saturated with potassium carbonate. The mixture was extracted three times with 20 ml of ether. The combined extracts were dried over sodium hydroxide. Ether was removed by distillation on a water bath, the other solvents by vacuum distillation. The remaining product could not be crystallised; it was dissolved in chloroform and passed down a neutral aluminium oxide column. The first fraction was collected and crystallised from petroeum ether.

b) Pyrrolidino benzenes.

A similar procedure with appropirate modifications was followed for pyrrolidino benzenes. Thus, pyrrolidine was refluxed for 1,5 hours with sodium amide and the reaction period was 12 hours. At the end when solvents were distilled, the tarry residue was refluxed with 40–50 ml of petroleum ether for 20 minutes. The etheral solution was filtered and boiled twice with small amounts of charcoal and evaporated to half volume. The impure crystals which resulted were eluted from a neutral aluminium oxide column by a 2:1 solution of petroleum ether and chloroform. The first fraction was recrystallised from petroleum ether.

RESULS AND DISCUSSION

In reactions with sodium piperidide disubstituted products were formed. 1, 2, 3, 5-tetrachlorobenzene gave a mixture of 2, 6-dipiperidino-1, 4-dichloro and 2, 4, 6-tripiperidino chlorobenzene. 1-chloro (or bromo or iodo)-2, 4, 6-triiodobenzenes did not give any product. The synthesized compounds are listed in Table I.

Table I

Substrate	Product	m.p. (*C)	Yield %	Spectrum No.
1-Bromo-2,4,6-Trichloro benzene	2,6-Dipiperidino-4-chloro bromo benzene	179–182	37.8	
1-Iodo-2,4,6-Trichloro benzene	2,6-Dipiperidino-4-chloro iodo benzene	170–173	20	
1-Chloro-2,4,6-Tribromo benzene	2,6-Dipiperidino-4-bromo chlorobenzene	170–172	37.8	1.2
1,2,3,5-Tetrabromo benzene benzene	2,6-Dipiperidino-1,4-dibromo benzene	180–183	35	
1-Iodo-2,4,6-Tribromo benzene	2,6-Dipiperidino-4-bromo iodo benzene	177	26.6	

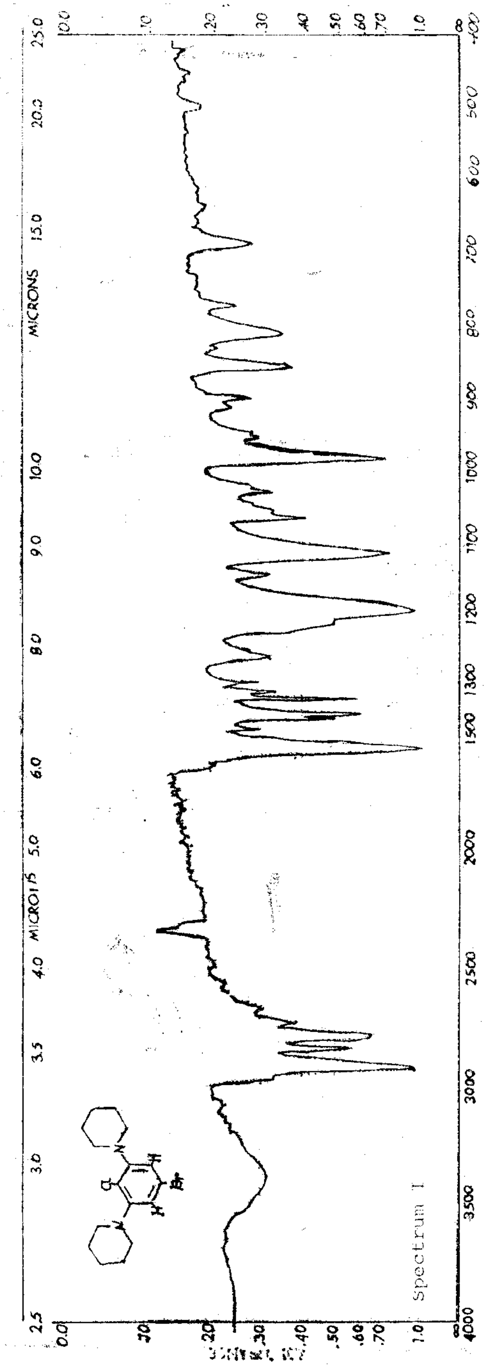
With sodium pyrrolidide, 1, 2, 3, 5-tetrachlorobenzene gave a mixture of tripyrrolidino chlorobenzene and 2, 6-dipyrrolidino-1, 4-dichlorobenzene; 2, 4, 6-trichloro bromobenzene gave a mixture of 2, 4, 6-tripyrrolidine bromo benzene and 1, 3-dipyrrolidino benzene; 2, 4, 6-trichloro iodobenzene gave a mixture of 2, 4, 6-tripyrrolidino iodobenzene and 1, 3-dipyrrolidinobenzene. 2, 4, 6-triiodo halogenobenzenes again did not react. The products are listed in Table 2.

Table 2

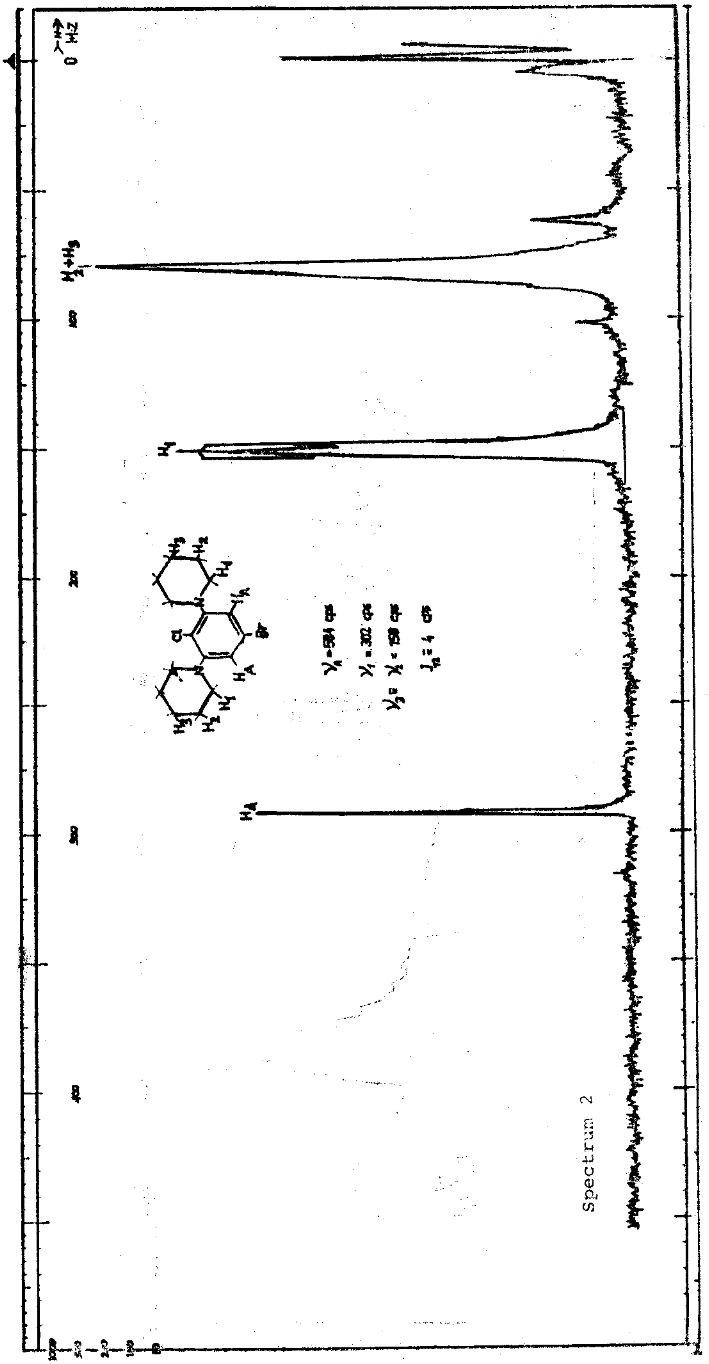
Substrate	Products	m.p. (*C)	Yield %	Spectrum No.
1-Chloro-2,4,6-tribromo benzenes	2,4,6-Tripyrrodidino chloro benzene	173–179	40	
1,2,3,5-tetrabromo benzene	2,6-Dipyrrolidino-1,4-dibromo benzene	172–175	34	3.4
1-Iodo-2,4,6-tribromo benzene	1,3-Dipyrrolidino benzene	94	92.6	5.6

As shown in the table 1, 3-dipyrrolidino benzene was obtained in good yield. The structure of this compound was elucidated by means of Zanger's NMR studies (6). NMR spectrums were recorded by a 100 M Hz spectrometer. Molecular weights wereserminet for all products.

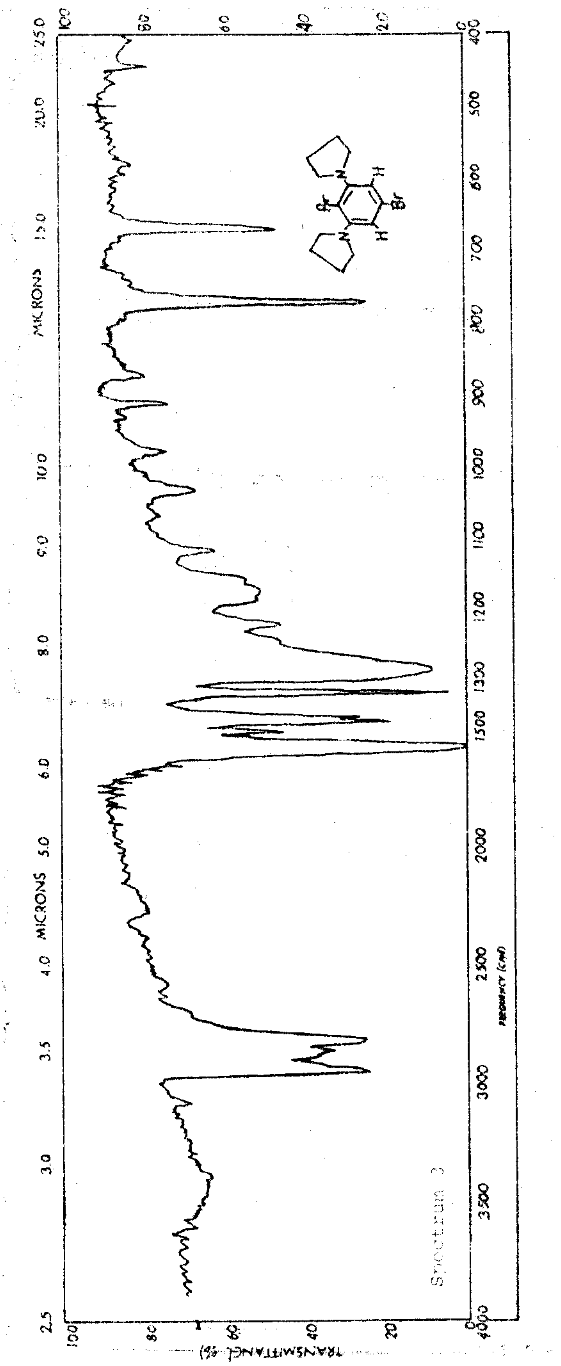
The products obtained in the present investigation were similar to those reported previously (1). A new observation was the formation of trisubstituted products from pyrrolidide. Reactions in pyrrolidide sometimes gave mixtures of products in which 1, 3-dipyrrolidino benzene was detected. This may have been due to the conversion of pyrrolidine to pyrrolidino benzene which was in fact formed on the main product in the reaction of 2, 4, 6-tribromo iodobenzene.


MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
9.0
10.0
15.0
20.0
25.0
4000
3500
3000
2500
2000
1500
1300
1200
1100
1000
900
800
700
600
500
400
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
Cl
N
H
Br

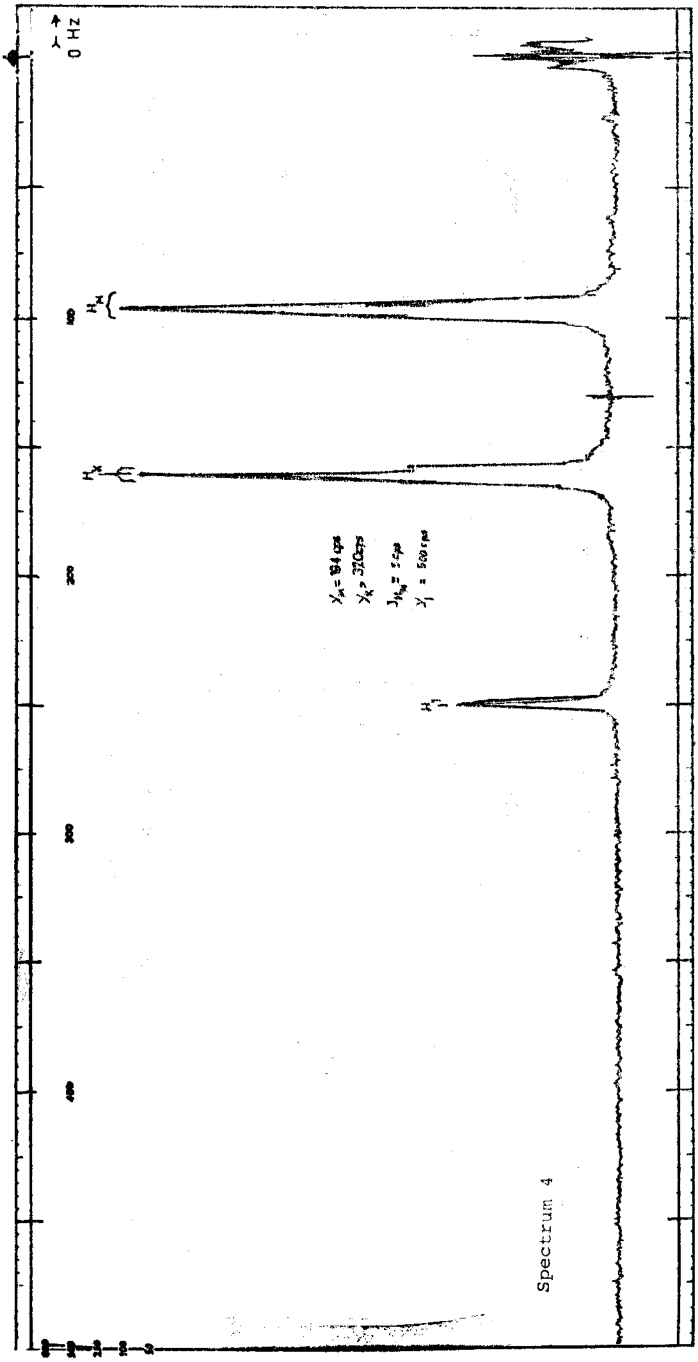
Spectrum I


0 Hz
100
200
300
400
H_2+H_3
H_1
H_A
Cl
Br
N
$\nu_A = 584$ cps
$\nu_1 = 302$ cps
$\nu_2 = \nu_3 = 158$ cps
$J_{12} = 4$ cps

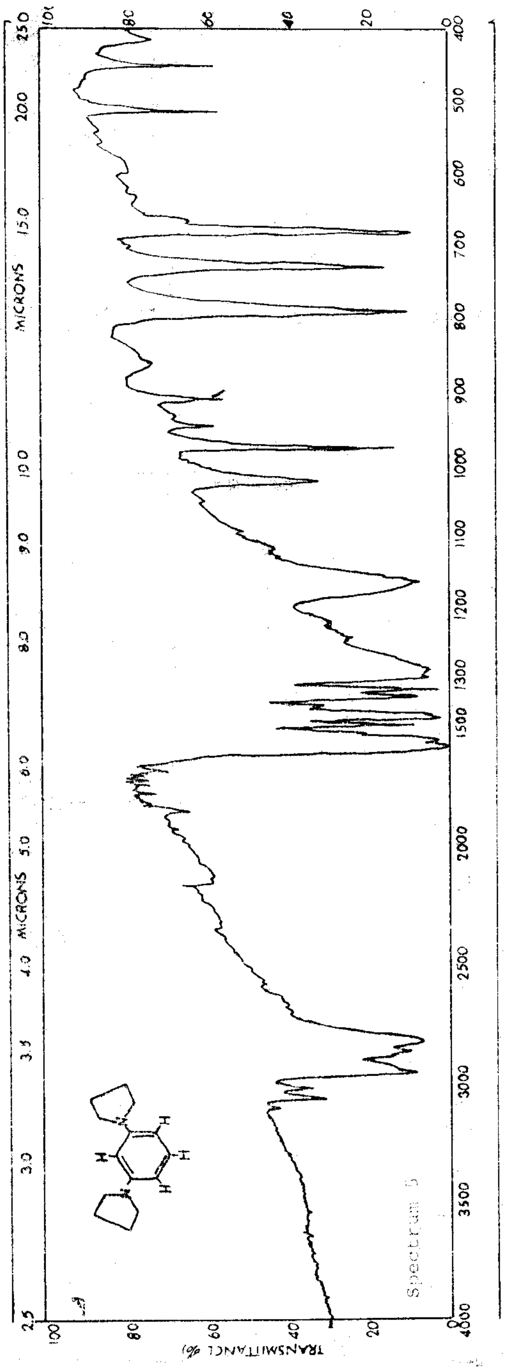
Spectrum 2


MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
9.0
10.0
15.0
20.0
25.0
4000
3500
3000
2500
2000
1500
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (cm-1)
TRANSMITTANCE (%)
100
80
60
40
20
0
N
N
Br
Br
H
H

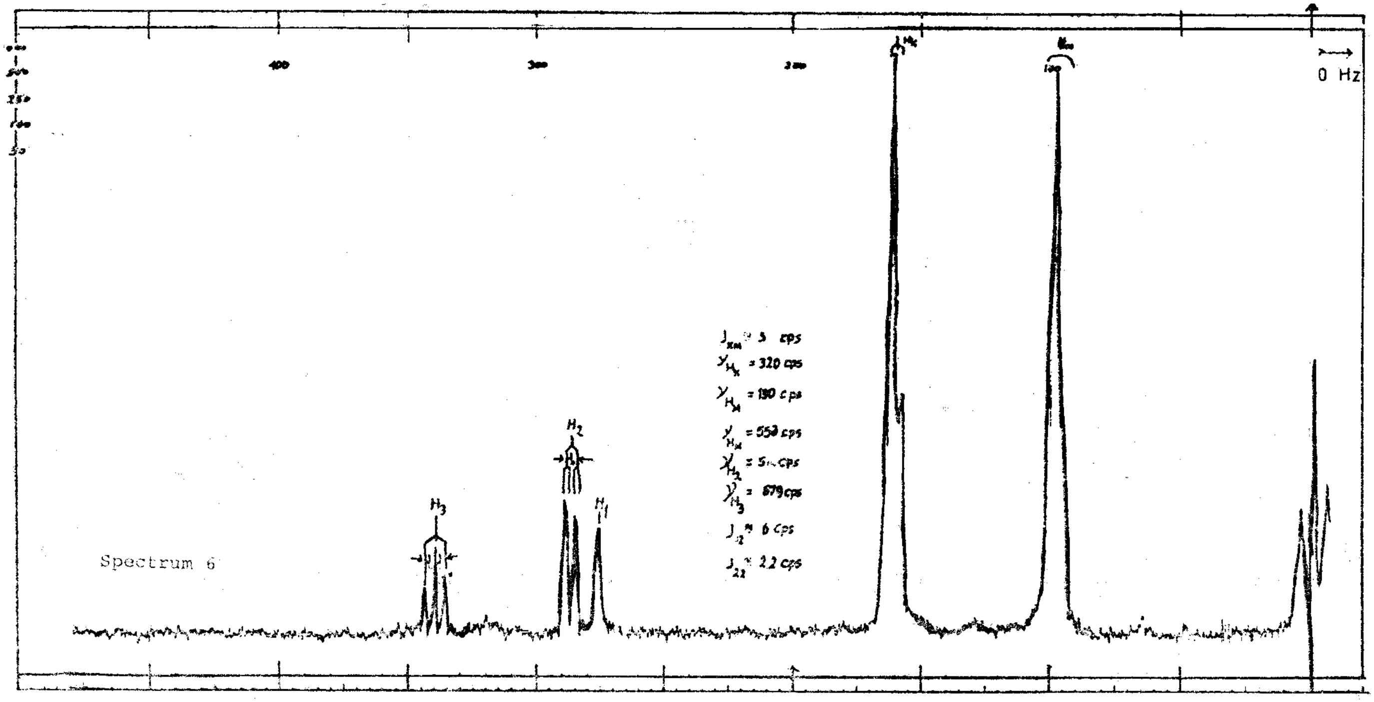
Spectrum 3


0 Hz
100
200
300
400
H_X
H_X
H_1
$\nu_A = 194$ cps
$\nu_X = 320$ cps
$J_{AX} = 5$ cps
$\nu_1 = 550$ cps

Spectrum 4


MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
9.0
10.0
15.0
20.0
25.0
4000
3500
3000
2500
2000
1500
1300
1200
1100
1000
900
800
700
600
500
400
100
80
60
40
20
0
TRANSMITTANCE %
H
H
H
H

Spectrum 5


0 Hz
100
200
300
400
500
250
100
50
H_X
H_M
H_1
H_2
H_3
$J_{XM} \approx 5$ cps
$\nu_{H_X} = 320$ cps
$\nu_{H_M} = 190$ cps
$\nu_{H_1} = 558$ cps
$\nu_{H_2} = 5..$ cps
$\nu_{H_3} = 679$ cps
$J_{12} \approx 6$ cps
$J_{22} \approx 2.2$ cps

Spectrum 6

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ÖZET

Bu çalışmada bazı 1,2,3,5-tetrahalojen benzenlerin sodyum piperidit ve sodyum piroliditle reaksiyonları denendi. Sodyum piperiditle yapılan reaksiyonlarda 2,6-dipiperidino-1,4-dihalojen benzenler elde edildi. Sodyum piroliditle di- ve tripirolidino benzenler ve reaksiyonların çoğunda karışımlar ele geçti. Karışımlarda 1,3-dipirolidino benzende gözlendi. Reaksiyonlardan birinde 1,3-dipirolidinobenzen ana ürün olarak iyi bir verimle elde edildi. Ürünlerin yapıları IR ve NMR spektrumları yardımıyla saptandı.

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