P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2009,(3), (1) :66-70

A New Method of Halogenation of Aromatic Compounds

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ARTICLE INFO

Received: 25 / 12 /2008
Accepted: 11 / 5 /2009
Available online: 14/6/2012
DOI: 10.37652/juaps.2009.15403
Keywords:
Method ,
Halogenation ,
Aromatic Compounds.

ABSTRACT

A halogenation of eleven aromatic compounds using a new method for iodination of activated aromatic compounds is presented. The reaction of one mole of aromatic compound with a mixture of one mole Potassium iodide and two moles Potassium sulfate in the presence of hydrochloric acid gives mono iodo aromatic compounds in high yields. The products have been identified by (I.R) spectrally and also by quantitative elemental analysis.

In conclusion, a convenient and versatile procedure for iodination of activated aromatic compounds has been reported. In this method, neither harmful reagents are used nor toxic residues are left after completion of the reaction. Thus, these iodination reactions are indeed, environmentally benign. In each case, mono iodination was identified with high yields.

Introduction

Iodo aromatics are useful materials or intermediates for the production of specially chemicals like medical drugs, agricultural chemicals, photosensitive materials, dyestuffs etc. They are also useful for the preparation of organometallic reagents and in metal catalysed coupling reactions which are applied for the preparation of complex molecules[1].

Apart form the applications; preparation of iodo organic is also an interesting one due to the least reactive nature of iodine among the halogen. Hence, iodination simply by molecular iodine is not possible; with most of the aromatic substrates, a powerful iodinating species more than iodine is required.

This is usually achieved by adding an oxidant like CrO_3[2], NO_2[3], $KMnO_4$[4]**,** Silversulphate[5] etc. with diiodine or by using an iodonium donating reagents like N-iodosuccinidimide**,**[6,7],iodinemononochloride, [8] NaI / Conc.H_2SO_4[9], etc. Most of these methods require toxic reagents and /or severe reaction conditions and by leaving hazardous waste make environmental problems.

Experimental

Instrumentation:

Appellate used were I.R.: Infrared Spectrophotometer, type (Philips), PU9706, Univ. Anbar, College of Sci. Dep. of Chem., C.H.N.: Element Analysis, Analyzer, Elmer 240 B-perken, Univ. Mutaa, College of Scince Dept. of Chemistry Jordan. and Purity of the iodoproduct was checked by TLC technique on silica gel-G coated aluminium plate, using hexane as eluent. The chromatogram was developed under a mixture of 1% vaniline and 5% ethanolic sulfuric acid as reagent.

procedure

A solution of o-Nitro aniline (3g, 0.022 mmol), Potassium iodide (3.52g, 0.022 mmol) and Potassium sulfate (5.94g, 0.044 mmol) was prepared in methanol (5mL) and 30 mL water. This mixture was treated at room temperature with 8 ml of hydrochloric acid over 2 h. After completion of reaction (TLC monitoring), the reaction mixture was extracted with diethylether (4x10 mL). The ether extract was washed with dilute Potassium thiosulphate (5%), water and dried over anhydrous K2SO4. Removal of solvent gave a residue which was purified through a short column packed with silica gel using hexane as eluent to afford P-iodo-o-

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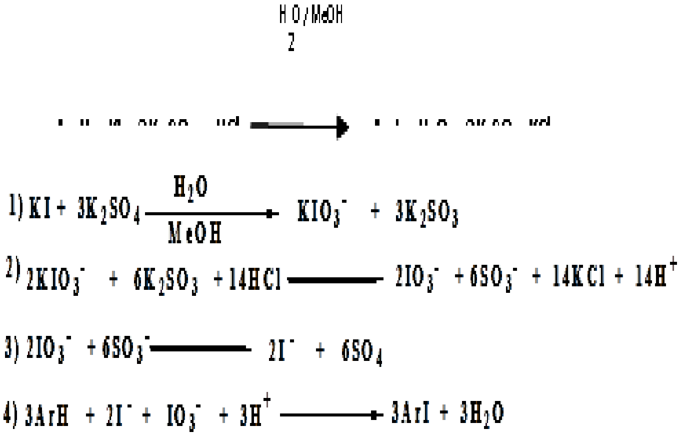
Nitroaniline (2.51g, 83.7%), mp. (219-220) C. Were diagnosed produced by Spectrally (I.R).
(See Table (1)(2)) in addition to the accurate quantitative elemental analysis.

In the same way to(eleven compounds) were prepared. (See. Table (1), and (2)).



$$1)\ KI + 3K_2SO_4 \xrightarrow[MeOH]{H_2O} KIO_3^- + 3K_2SO_3$$

$$2)\ 2KIO_3^- + 6K_2SO_3 + 14HCl \longrightarrow 2IO_3^- + 6SO_3^- + 14KCl + 14H^+$$

$$3)\ 2IO_3^- + 6SO_3^- \longrightarrow 2I^- + 6SO_4$$

$$4)\ 3ArH + 2I^- + IO_3^- + 3H^+ \longrightarrow 3ArI + 3H_2O$$

scheme 1.

Careful product analysis(TLC, elemental analysis, I.R.) confirmed the formation of P-Iodo o-nitro aniline with very good yields. To generalize this iodination reaction of arenes, different activated aromatic substrates were chosen and the reactions were carried out under similar reaction conditions (Table 1).As expected, all the substrates undergo
iodination reactions and delivered mono iodo product in good yields.

In this iodinating system, the possible iodination reactions of aromatic compounds are shown in **scheme 1**. When Potassium iodide is treated with Potassium sulfate in the presence of hydrochloric acid, iodide anion is liberated. The iodide anion thus formed undergoes oxidation reaction with iodide and furnishes more reactive electrophilic iodonium ion which can affect aromatic iodination.

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Results and Discussion

Initially, the test reaction was carried out on o-Nitro aniline with Potassium iodide and Potassium sulfate in the presence of hydrochloric acid in aqueous methanol according to the stoichiometry. Fig. (1) and **scheme 1**.

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Table (1) Characterization data of Prepared (1-11)

No.	Substrate	Product	(M.Wt.)	M.P/C^0	Yield%	Analysis Clcd./ (Found)			
						C%	H%	N%	I%
1	O-nitroaniline	P-Iodo O-nitro aniline	$C_6H_5N_2O_2I$ (263.98)	219-220	83.7	27.30 27.01	1.89 1.30	10.61 9.88	48.07 47.09
2	O-nitrophenol	P-Iodo O-nitro phenol	$C_6H_4NO_3I$ (264.97)	211-210	91.4	27.20 26.90	1.51 1.02	5.29 5.01	47.89 46.82
3	M-nitrotoluene	P-Iodo M-nitrotoluene	$C_7H_6NO_2I$ (262.98)	259-260	88.0	31.97 31.68	2.28 2.09	5.33 5.20	48.25 48.11
4	M-Methylaniline	P-Iodo M-Methylaniline	C_7H_8NI (232.98)	238-239	89.2	36.08 35.98	3.43 3.40	6.01 5.96	54.47 54.38

5	P- Methylaniline	O-Iodo P- Methylaniline	C_7H_8NI (232.98)	215-216	79.8	36.08 36.01	3.43 3.14	6.01 5.77	54.47 54.26
6	Naphthalene	α-Iodo naphthalene	$C_{10}H_7I$ (254.00)	293-294	88.6	47.28 47.10	2.76 2.42	—	49.96 49.52
7	Methylnaphthale	α-Iodo β - Methalnaphthal	$C_{11}H_9I$ (268.01)	150-151	90.2	49.29 48.92	3.36 3.12	—	47.35 47.25
8	Toluene	P-Iodotoluene	C_7H_7I (217.60)	177-178	87.0	38.64 38.33	3.22 2.98	—	58.32 57.89
9	Banzoicacid	M-Iodo benzoicacid	$C_7H_5O_2I$ (247.97)	152-153	88.4	33.90 33.80	2.02	—	51.18 50.91
10	P-Nitrotoluene	O-Iodo P- nitrotoluene	$C_7H_6NO_2I$ (262.98))	54-55	85.5	31.97 31.66	2.28 2.15	5.33 5.23	48.25 47.99
11	Aniline	P-Iodo aniline	C_6H_6NI (218.87)	67-68	87.3	32.91 32.55	2.74 2.62	6.40 6.16	57.95 57.49

Table (2) IR. Spectra of Prepared (1-11)

NO.	N-H *cm*$^{-1}$	C-I *cm*$^{-1}$	C-N cm^{-1}	C-C cm^{-1}	C=C aromatic	C-H cm^{-1}	Other			
							group	cm^{-1}	group	cm^{-1}
1	3470-3390	525	1295	1100-900	1610-1500	810	NO_2	1450,1398	OH	3425
2	-------	510	1308	1210-980	1550-1470	790	NO_2	1400,1390	CH	3510
3	-------	550	1290	1050-910	1530-1560	810	NO_2	1490,1355	CH	3100
4	3410-3310	550	1255	1040-930	1640-1590	810	-------	-------	CH	3200
5	3480-3380	560	1325	1050-900	1630-1510	810	-------	-------	CH	3200
6	-------	510	-------	1010-950	1600-1500	790	-------	-------	-------	
7	-------	520	-------	1020-970	1620-1500	800	-------	-------	CH	3100
8	-------	510	-------	1010-980	1600-1500	850	-------	-------	CH	3100
9	-------	550	-------	1090-950	1600-1590	820	OH	2940	C=O	1700
10	-------	550	1292	1050-910	1530-1560	810	NO_2	1490,1368	CH	2900
11	3190,3290	500	1298	1090-910	1610-1500	810	-------	-------	-------	3200

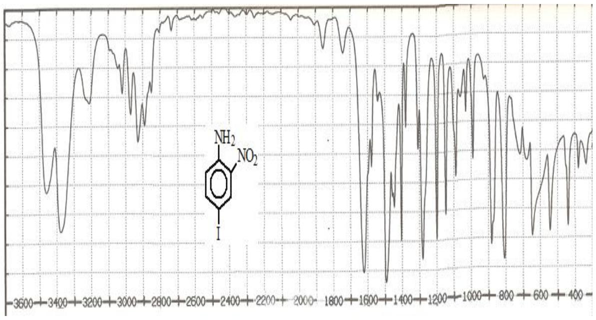


Fig. (1)

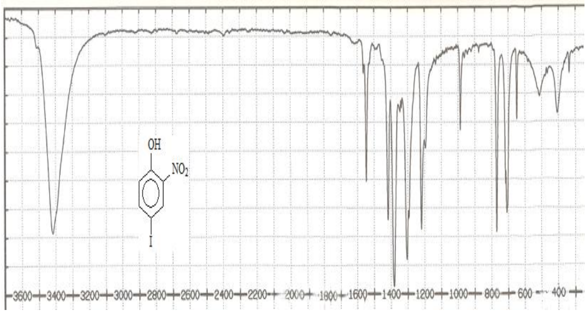
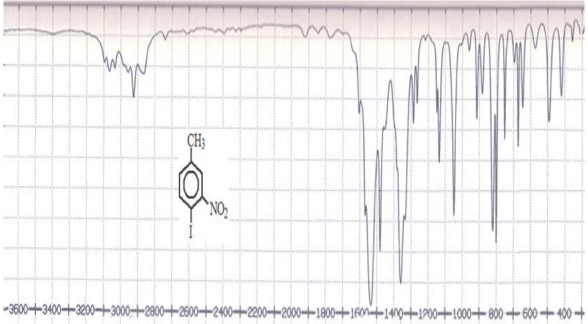


Fig. (2)



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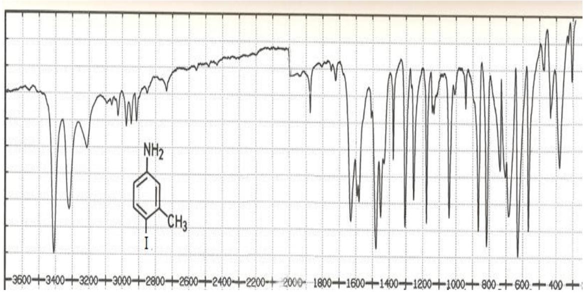

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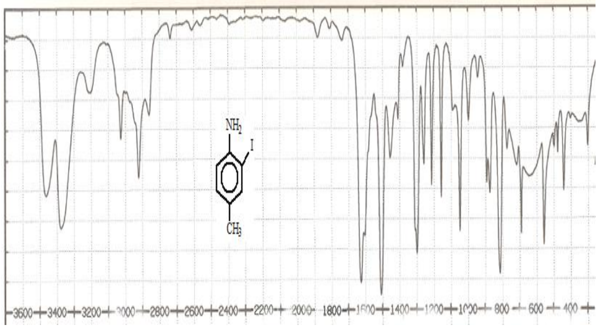

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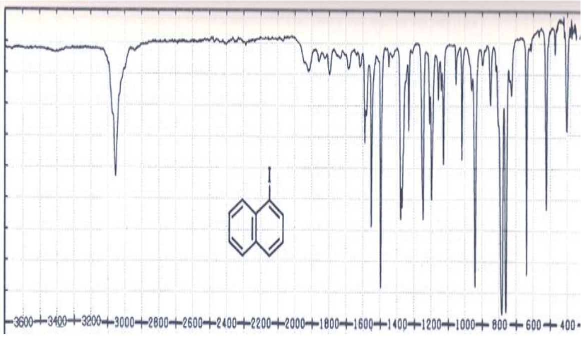

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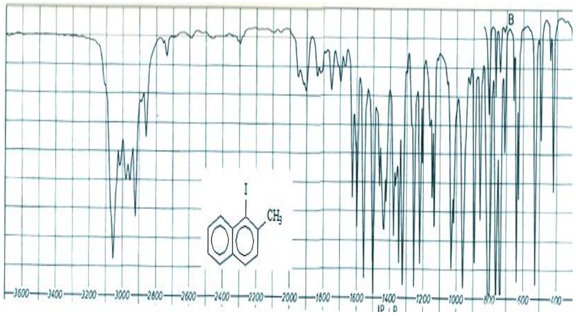

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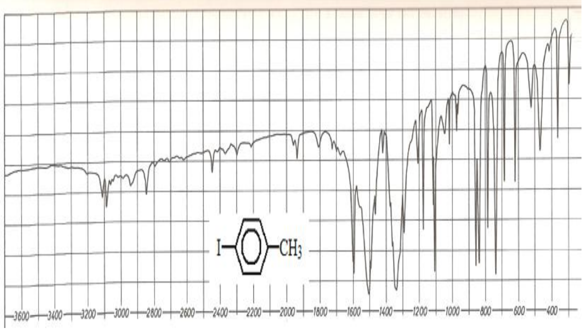

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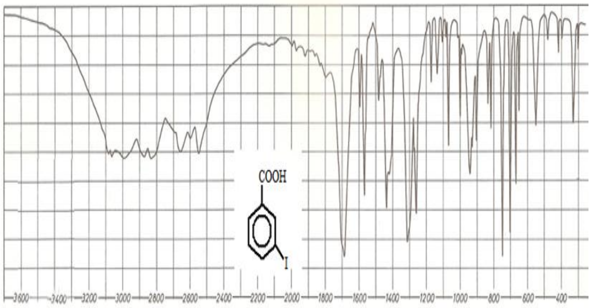

Fig. (9)

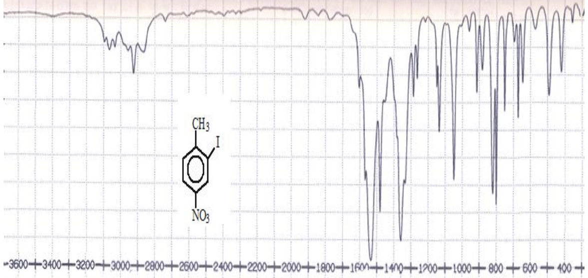

Fig. (10)

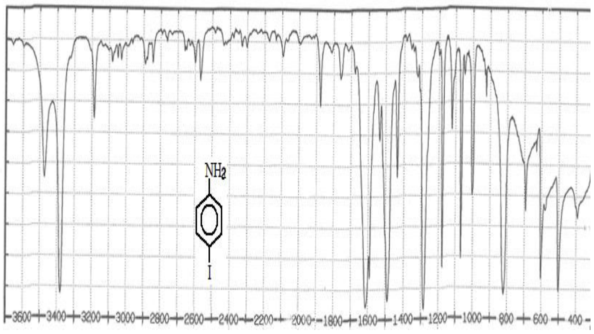

Fig. (11)

P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
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طريقة جديدة لهلجنة المركبات الاروماتية

مروان محمد فرحان

الخلاصة

تم هلجنة احدى عشر مركب اروماتي بوساطة اليود، وبصورة رئيسية استخدمت طريقة جديدة لهلجنة المركبات الاروماتية، حيث تم تفاعل واحد مول من المركب الاروماتي مع مزيج مكون من واحد مول يوديد البوتاسيوم مع مولين من كبريتات البوتاسيوم بوجود حامض الهيدروكلوريك، واعطى مركبات احادية اليود وبنسبة منتوج عالية، وتم تشخيص الناتج طيفيا بطيف الـ(I.R) والتحليل الكمي للعناصر.

ونتيجة لذلك تعتبر هذه الطريقة طريقة عمل سهلة ومتعددة الاستعمال ليودنة المركبات الاروماتية . ولم تستعمل بهذه الطريقة أي كواشف ضارة ولم ينتج اويترك مركبات جانبية سامة بعد اكمال التفاعل ، وبهذا التفاعل اليودنة في الحقيقة تفاعل نقي وفي كل حالة ينتج مركب احادي اليود.